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Bromide Removal from Surface Waters by Silver Impregnated Activated Carbon

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REMOVAL OF BROMIDE FROM SURFACE WATERS USING SILVER IMPREGNATED ACTIVATED CARBON

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ABSTRACT

Bromide is a precursor of disinfection by-products (DBPs) during potable water treatment, because it causes the formation of brominated DBPs that are more cyto- and geno-toxic than their chlorinated analogues. Due to the potential health risks of DBPs, the United States Environmental Protection Agency (USEPA) has been imposing increasingly stringent regulations for controlling the DBPs. Therefore, removal of bromide ions from source waters becomes critical for controlling the DBPs formation. In my study, it was hypothesized that silver impregnated activated carbon (SIAC) can be a promising adsorbent for bromide removal from water. The main research objectives of this study were to: (i) conduct a systematic investigation for developing a fundamental understanding of SIAC preparation for enhanced removal of bromide from natural waters and (ii) investigate the impact of aqueous background composition (i.e., the presence of natural organic matter and competing anions like chloride, nitrate and sulfate) on the bromide uptake.

The study had three sub-objectives: The first objective was to determine the optimum silver impregnation protocols and assess the role of carbon characteristics (e.g., activated carbon characteristics, silver impregnation techniques and pre-oxidation conditions) to produce SIACs to remove Br^- from natural waters; and evaluate their effectiveness for Br^- removal.

The second objective was to evaluate the developed SIACs at typical water treatment conditions. This task involved mainly investigating the competing anions (e.g.

Cl^-) and NOM and the background matrix effect in natural water samples (e.g. pH, TOC, SUVA, presence of alum during coagulation/flocculation, etc.)

The third objective was to evaluate the impact of selected SIAC for DBPs formation control (i.e., THMs control) in natural waters.

Several combinations of preparation pathways were employed to prepare SIACs (AC pre-oxidation with 10N and 15.7N nitric acid at 90 ℃ and 160 ℃ followed by silver impregnation with 0.1, 0.5, 1.5M silver nitrate) and to examine the adsorption of bromide from natural waters. Pre-oxidation with 15.7N HNO_3 at 90 ℃ and silver impregnation with 0.5M $AgNO_3$ were found to be an appropriate preparation method. In addition, two commercially available SIACs (1.05% and 4.03% silver contents by weight) showed significantly higher bromide uptakes then the virgin activated carbon (AC) in distilled and deionized water (DDW). The enhanced bromide uptake was attributed to the presence of silver species on the carbon surface. The low silver bromide solubility ($K_{sp}AgBr = 5.2\times10^{-13}$), and large carbon surface area enabled the SIACs to adsorb bromide from water solution. However, the removal efficiency was affected by the background aqueous conditions (e.g. Cl^- concentration, presence of NOM, and other background matrix), silver impregnation process (e.g. silver content, with/without pre-oxidation of virgin AC) and AC characteristics (e.g. surface area, oxygen content). The adsorption experiments showed that SIACs with higher silver contents and larger carbon surface areas exhibited a high degree of bromide removal. The Cl^- and natural organic matter (NOM) competition and the water background matrix were important interferences for Br^- removal by SIACs. Less Br^- removal was observed as the Cl^-

concentration in the background solution increased; the decreased removal was mainly due to the Cl^- competition because the Cl^- and Br^- competed for silver in the SIAC carbon pores. Br^- removal was inhibited in the presence of 2.5 mg/L NOM, which can be attributed to the NOM competition and the pore blockage.

DEDICATION

I would like to dedicate this to my parents and friends, for their understanding and love.

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Firstly, I would like to express my sincere appreciation to my advisor. Dr. Tanju Karanfil, for his guidance, patience and support during my graduate study, and my committee members, Dr. Cindy Lee and Dr. David Ladner, for their insight and expertise. Special thanks to Onur Guven Apul, who is a PhD student in Dr. Karanfil's research group, for both his valuable insights in this study and his continuous help with carbonaceous adsorbents characterization works; also thanks to Shanna Estate who is a phD student in Dr. Brian Powell's research group for her help with the carbon silver content measurement and Dr. Brian Powell for providing the ICP-MS equipment.

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LIST OF ABBREVIATION

AC	Activated Carbon
20B	20B Activated Carbon
BET	Brunauer-Emmett-Teller
BIF	Bromine incorporation Factor
CH	Charleston
DBPs	Disinfection Byproducts
DBCM	Dibromochloromethane
DCBM	Dichlorobromomethane
D/DBPR	Disinfectants/Disinfection Byproduct Rule
DDW	Distilled and Deionized Water
DOC	Dissolved Organic Carbon
EDA	Electron Donor Acceptor
Edisto	Edisto River
F400	F400 Activated Carbon
GAC	Granular Activated Carbon
GC	Gas Chromatography
HAA	Haloacetic Acid
HD3000	HD3000 Activated Carbon
HW	Lake Hartwell
IC	Ion Chromotography
K_{sp}	Solubility Product

MB	Myrtle Beach
MW	Molecular Weight
NF	Nanofiltration
NOM	Natural Organic Matters
PAC	Powdered Activate Carbon
pH	$-\log[H^+]$
pH_{PZC}	pH of Point of Zero Charge
ppb	Parts Per Billion
SIAC	Silver Impregnated Activated Carbon
SIAC-Cl	Silver-Chloride Impregnated Activated Carbon
SSA	Specific Surface Area
SUVA	Specific Ultraviolet Absorbance
TBM	Tribromomethane
TCM	Trichloromethane
THM	Trihalomethane
TOC	Total Organic Carbon
TOX	Total Organic Halides
TTHM	Total Trihalomethanes
USEPA	United States Environmental Protection Agency
UFC	Uniform Formation Condition
WC800	WC800 Activated Carbon

CHAPTER ONE

INTRODUCTION

Bromide (Br^-) is ubiquitous in natural waters especially in waters impacted by anthropogenic activities including discharge of treated or untreated wastewaters, the releases from coal-fired power plants and hydraulic fracturing operations, and sea water intrusion. Although Br^- in drinking water has no direct public health ramifications, it can lead to formation of regulated disinfection byproducts (DBPs) during water treatment, such as bromate (BrO_3^-), brominated trihalomethanes (THM) and brominated haloacetic acids (HAA). BrO_3^-, isformed during ozonation, while brominated THMs and HAAs can be formed during chlorination. Brominated DBPs are more cyto- and geno- toxic than their chlorinated analogues [Plewa et al., 2008]. The potential health risks of DBPs have raised concerns, as a result increasingly stringent regulations are imposed for some DBPs under the Disinfectants/Disinfection Byproduct Rule (D/DBPR) of United States Environmental Protection Agency (USEPA) [Richardson et al., 2008].

Numerous materials, including metal impregnated sorbents (e.g. zeolite and alumina), activated carbons (ACs), activated carbon fibers, and anion exchange resins have been evaluated for removal of Br^- from water [Amy et al., 1999; Prados et al., 1993]. However, there is as yet no well-established technology to control Br^- at drinking water treatment plants.

Silver impregnated activated carbon (SIAC) is obtained by impregnation of AC surface by silver. The porous structure and large surface area of ACs make them a particularly useful support media for silver impregnation. In this study, it was

hypothesized that SIACs can be developed as novel adsorbents for selective removal of Br^- from water and can be used to reduce the formation of brominated DBPs at the water treatment plants and distribution systems.

The main research objectives of my study was to: (i) conduct a systematic investigation for developing a fundamental understanding of SIAC preparation for enhanced removal of bromide from natural waters, and (ii) investigate the impact of aqueous background composition (i.e., the presence of natural organic matter and competing anions like chloride, nitrate and sulfate) on the bromide uptake.

CHAPTER TWO

LITERATURE REVIEW

2.1 Activated Carbon

Activated carbon is a heterogeneous and porous adsorbent with very high capacity for adsorbing high quantities of contaminants from water. The structure of AC is commonly considered to be composed of randomly orientated crystallites, which are extensively interconnected by tetragonally bonded carbon cross-links [Smisek et al., 1970]. The crystallites are parallel layers of trigonally covalent bonded carbon. The distance and voids between the crystallites compromise the pores. The ability of activated carbon to adsorb large quantities of materials is directly related to its porous structure and extraordinarily large surface area [Summers et al., 1988; Baker et al., 1992]. The physical characteristics of ACs are commonly described by specific surface area (SSA), pore size, pore volume and pore size distribution.

According to the IUPAC (International Union of Pure and Applied Chemistry) classification, carbon pores are classified as micropores (pores smaller than 20Å), mesopores (pores from 20Å to 500Å) and macropores (pores larger than 500Å). The micropores contribute mostly to the large surface area of AC and the adsorption of small size molecules. Macropores have less specific surface area, thus contribute less to adsorption, but they are important for molecular access to micropore regions. Due to higher adsorption free energies, compounds are preferentially adsorbed in pores with similar dimensions because of multiple contact points between the compounds and carbon surfaces [Karanfil et al., 1999; Pelekani et al., 1999].

The chemical nature of activated carbon is affected by its precursor material and activation process. Generally, 5-20% by weight of activated carbon consisted of non-carbon elements, with metal and surface bound oxygen as the major components [Sontheimer et al., 1988]. The surface oxygen-containing functional groups occurred at the crosslinks and edges of crystallites [Puri, et al., 1980]. Therefore the edge atoms of the crystallite were approximately 20 times more reactive than those of the basal plane of carbon [Henning, et al., 1962]. Researchers have identified the existence of carboxylic, hydroxyl, carbonyl, lactone and quinone groups on the activated carbon surface [Garten et al., 1957; Boehm, 1974; Puri, 1970; Coughlin and Ezra, 1968].

Activated carbon adsorption was initially employed for taste and odor control in drinking water treatment in the 1920s [Baylis et al., 1929]. With the implementation of the Safe Drinking Water Act, it has been commonly used to remove organic compounds of health concern, in addition to odor and taste control [Culp and Clark, 1983]. AC can be produced from various carbonaceous raw materials, including sawdust, peat, lignite, coal, cellulose residues, hardwoods, spent ion exchange resins, used automobile tires, nut shells and corn cobs [Sanga et al., 1975; Young et al., 1996; Teng et al., 2000]. The raw materials are prepared and activated by either a stream of activating gas (e.g. carbon dioxide) or a chemical agent (e.g., phosphoric acid) to produce highly porous activated carbon [Krczil, 1937; Dubinin et al., 1949; Suzuki, 1954]. The pore structure of activated carbon is determined by the raw materials, the type of activating agent, the activation temperature and time [Hashimoto et al., 1979].

2.2 Silver Impregnated Activated Carbon

There are several silver or metal impregnations of activated carbons including 1) ion exchange, 2) excess solution, 3) incipient wetness, 4) physical deposition on vapors, 5) chemical vapor deposition, and 6) precipitation [Radovic et al., 1997].

Ion exchange is one of the most widely used methods for metal impregnation. Activated carbon is equilibrated with a solution of metal ion salt, to exchange surface protons with the metal ions [Ross et al., 1985; Richard et al., 1989; Scardi and Antonucci, 1993]. This method is very sensitive to the nature of the carbon surface. The availability of a sufficient number of the proper acidic groups (e.g. carboxylic) is a crucial factor. As a result, development of these functionalities prior to the ion exchange stage of the process is highly recommended. After the ion exchange step, carbons are washed and filtered to remove the metal cations not strongly-adsorbed on the carbon surface. High degree of dispersed metal can be loaded on the carbon by ion exchange.

Excess solution is a common and easy impregnation method. Carbon is mixed with a solution of metal precursor then solvent is evaporated, or the carbon is separated from the solution by decantation or filtration before drying of the sample [Aika et al., 1972; Zaidi, 1987, Shaikhutdinov 1995]. The major difference between excess soltion and ion exchange is that the carbon is not washed before drying. Part of the metal is adsorbed on the carbon surface, and part of it may simply be retained within the pores and the space between the carbon particles. As a result, impregnated carbon may contain both strongly adsorbed (i.e., ion exchanged) and weakly adsorbed metals (i.e., metal ions retained in the pore space).

Incipient wetness impregnation is also known as pore volume impregnation. The method requires knowledge of the carbon pore volume before impregnation. The metal precursor solution is prepared at the concentration corresponding to the desired metal loading. The solution is added to the carbon drop by drop with vigorous stirring until the last drop, suggesting the entire pore volume has been filled with metal cations [Louwers and Prins, 1992; Potoczna-Petru and Krajczyk, 1995]. After impregnation in the carbon pores, the silver can be reduced or oxidized through various methods to obtain desired species.

In this study, the ion exchange method was applied. The other three methods were not so widely used and not much related to this research; as a result, no further description was provided here. In brief, the powdered activated carbon (PAC) is mixed in a silver nitrate salt (e.g. $AgNO_3$) solution and put in dark overnight for silver impregnation. Silver ions associate with the graphitic surface of activated carbon and form either inner or outer sphere complexes. The hydroxyl groups in the carbon surface act as σ-electron donor ligands in the inner sphere complexation, and the counter ions form ionic complexes in the outer sphere complexation. Outer sphere complexes are less stable due to electrostatic (ionic) bonding instead of chemical bonding [Jia et al., 1998]. In addition, p-orbital electrons on the graphitic surface of activated carbon can also attract Ag^+ regardless of the surface charge. After attachment to carbon surface, Ag^+ is reduced to elemental Ag by the donation of electrons from carbon surface. The reduced silver on carbon surface may form clusters that lessen the contact with anions, which in turn results in less Br^- removal [Davidson 1994].

The SIACs produced from different virgin ACs are expected to maintain a similar level of the original carbon texture (similar carbon surface area, pore size distribution), and to be capable of removing Br^- from water solutions through silver halide precipitation reactions ($K_{sp}= 5.2\times10^{-13}$ for AgBr). Pre-oxidation of AC can help with silver impregnation, thus Br^- adsorption performance by SIACs. The conditions for SIAC preparation from different AC materials need to be experimentally determined.

2.3 Importance of Removing Bromide

Bromide is ubiquitous in natural waters and concentrations range from 2 to 3000 μg/L, (see Table 2.1 [Amy et al. 1993; Legube et al. 1993]). Waters affected by sea water intrusion as well as anthropogenic activities (i.e. untreated and treated wastewater discharges, the residue within process/flowback waters from hydraulic fracturing operations, and discharges from air pollution control equipment of coal-fired power plants) contain elevated levels of Br^- concentrations [Krasner et al., 1989; Amy et. al., 1993; McCuire et. al., 2002]. Although Br^- in drinking water has no direct adverse public health effects, its presence can cause the formation of regulated DBPs such as BrO_3^-, brominated THMs, brominated HAAs during water disinfection [Li, et al., 1995; Hong et al., 2012, Welch 2012].

Table 2.1 Occurrence of Br^- in Natural Waters

Source	Number of Sources	Br^- range (μg/L)	Average Br^- (μg/L)
U.S. rivers	35	10 – 3000	110
European rivers	13	20 – 1040	150
European groundwaters	5	48 – 209	102
European lakes	6	12 – 184	99
U.S. rivers	29	3 – 426	101
U.S. lakes	34	3 – 322	38
U.S. groundwaters	37	2 – 429	96
U.S. coastal areas	11	50 - 400	210
US water treatment plant influents	500	<10 - 2230	69

Brominated DBPs are formed by the reactions of organic and inorganic precursors with oxidants/disinfectants used in water treatment plants. Heterogeneous mixtures of various organic molecules in natural waters such as natural organic matter (NOM), and Br^- in natural waters can react with disinfectants (e.g., chlorine, chlorine dioxide, chloramine, ozone) that are utilized in drinking water treatment. In addition, chlorine, HOCl and HOBr forming in water may react with NOM to form different types of organic halides, also known as total organic halides (TOX). Due to the potential health risks of DBPs, USEPA has been imposing increasingly stringent regulations under the D/DBPR. Stage 2 of D/DBPR requires utilities to comply with the maximum contaminant levels (MCLs) of total THM (i.e., chloroform, bromodichloromethane, dibromochloromethane, and bromoform) and the sum of five HAA species (i.e., chloroacetic acid, dichloroacetic acid, trichloroacetic acid, bromoacetic acid, and dibromoacetic acid) at 80 and 60 μg/L, respectively, for the running annual average at individual locations in distribution system according to U.S. EPA (2006). Controlling the

bromide concentration in natural waters is important to reduce the source of brominated DBP precursors.

2.4. Existing Br^- Removal Techniques

Several techniques have been investigated for removing Br^- from natural waters. Electrochemical treatment is sufficient to remove Br^- through oxidation, but the byproducts generated in the process need further treatment. [Amy et al., 1999] Adsorption of Br^- on metal (aluminum or iron) hydroxide flocs during coagulation was shown to remove 15-20% of initial Br^- from water at an unfeasibly high coagulant doses (200 mg/L), and the sludge of the process was a serious concern [Amy et al., 1999]. Co-precipitation with magnesium hydroxide can remove 17-26% of initial Br^- from water during softening, but required very high doses (200 mg/L) of lime [Prados et al., 1993]. Nanofiltration (NF) can remove Br^-, the rejection of Br^- ranges from 3% to 10% by a slightly negative or negative membrane surface charge, high rejection of total organic carbon (TOC) coupled to low removals of Br^- by some NF membranes was reported. In addition, the high cost limits the full-scale application [Chellam et al., 2000]. Adsorption on activated carbon can remove some Br^-, but rapid breakthrough times (e.g., bed volumes 1000 for an empty bed contact time of 4 to 10 minutes) have been observed. Though ion exchange is effective in removing Br^- from water, especially after coagulation and flocculation for low dissolved organic carbon (DOC) groundwaters, the presence of competing anions and NOM, and the cost of integration to full-scale processes limit its use [Amy et al., 1999]. Silver loaded activated carbon has been discussed for its ability to remove halogens (e.g., iodide) from aqueous solutions

[Hoskins et al., 2002]. In this study, it was hypothesized that SIACs adsorption can be also effective in removing Br^- from water, which can be easily applied in existing water treatment plants, before/after coagulation/flocculation process. However, the presence of competing anions and NOMs may affect the performance of Br^- removal by SIACs.

2.5 Adsorption of Br^- by SIACs

Previous studies show that sorbent surfaces may be tailored to enhance the removal of specific environmental contaminants (e.g. cyanide, arsenic, and metals) [Choi et al., 1994; Dixon et al., 1978; De Jong et al., 1993; Rajakavic 1992]. AC is a widely used adsorbent and the AC surface can be tailored for the removal of Br^- from water.

Silver ions form insoluble precipitates with halides and enhance their adsorption by SIAC. The following reactions show the precipitation of silver salts and their prospective solubility constants (K_{sp}).

$Ag^+ + Br^- \rightarrow AgBr_{(s)}$, $K_{sp}= 5.2 \times 10^{-13}$ (Reaction 1)

$Ag^+ + Cl^- \rightarrow AgCl_{(s)}$, $K_{sp}= 2.8 \times 10^{-10}$ (Reaction 2)

Reaction 1 can also take place on the surface of SIAC during the adsorption of Br^- in water. The reaction is expected to occur when Br^- ions from the water solution enter the carbon pores and contact with the available silver ions on the activated carbon surface. Reaction 2 is the precipitation of AgCl that may occur in the presence of chloride in water. Due to the much lower K_{sp} of AgBr than AgCl, the precipitation of AgBr is more

likely to take place on the carbon surface; however this will likely to depend on the chloride concentration and chloride to bromide ratio in water.

$$AgCl_{(s)} + Br^- \rightarrow AgBr_{(s)} + Cl^- \qquad \text{(Reaction 3)}$$

Reaction 3 shows the ion exchange between Br^- and AgCl(s) in water solution, which means the Cl^- inside the $AgCl_{(s)}$ is still exchangeable with free Br^- in aqueous condition. However, due to the abundance of Cl^- in sources waters, the much higher Cl^- concentration than Br^- can make reaction 3 reverse.

In previous study by Hoskins [2001], it was observed that silver impregnated activated carbons (SIACs) were effective in removing I^- from DOE waste streams (see Reaction 4). Reaction 4 shows the precipitation of I^- with Ag^+, because of the low K_{sp} of $AgI_{(s)}$, I^- can be precipitated out.

$$Ag^+ + I^- \rightarrow AgI_{(s)}, \quad K_{sp} = 8.5 \times 10^{-17} \qquad \text{(Reaction 4)}$$

$$O_{2(aq)} + 4H^+_{(aq)} + 4Ag^0_{(s)} \rightarrow 4Ag^+_{(aq)} + 2H_2O \qquad \text{(Reaction 5)}$$

In studies conducted by Hoskins [2001], he observed that the removal and sequestration of I^- by SIAC is an interplay between I^- concentration, silver content of activated carbon, and pH. First, metallic silver on SIAC is oxidized under oxic aqueous conditions (see Reaction 5), and the carbon surface acts as a catalyst. Reaction 5 shows the metallic silver is converted to Ag^+ and becomes available to dissolved I^- in water solution. Then, when silver ions become available, silver iodide precipitation can occur. As silver ions are removed by precipitation with iodide, a driving force for additional silver oxidation is created until all available silver reacts with iodide. The precipitation of Br^- by SIAC is the same mechanism as the precipitation of I^-.

2.6 The Effect of Water Chemistry

There are several anions in natural waters such as chloride, sulfate, and nitrate along with the natural organic matters (NOM) that can impede Br^- removal. Among them, Cl^- is the most competitive and interfering ion for Br^- removal. Because in natural waters, Br^- exists at concentrations ranging from 2 to 3000 μg/L, while Cl^- has 50 to 1000 time higher concentration. When the Br^- ions are overwhelmed by the Cl^- in the water, the chances for Br^- to adsorb on the available Ag^+ are largely decreased. Therefore, the high Cl^- concentration waters are among the most challenging waters for SIAC treatment.

Sanchez polo et al. [2006, 2007] reported that the Ag-doped activated carbon aerogels remove Br^-, but decrease of Br^- removal was observed in the presence of NOM. The decreased could be due to blocking of pores by dissolved organic matters or NOM molecules could compete for Ag coated surface sites. NOM, which is inherent in natural waters, and typically has a net negative charge at neutral pH values, may either directly compete for adsorption sites or block the inner pores of carbon due to its macromolecular structure. In addition, the Br^- removal capacity of Ag-aerogels in the presence of Cl^- was decreased ~35%, which indicates a competition between halides for aerogel sorption sites. Moreover, there is a more severe competition at higher Cl^- concentrations (40 mg/L), but there was still a substantial amount of Br^- removal even under Cl^- competition. However, they did not distinguish the impact of Cl^- from the impact of NOM since the selected natural water had both constituents, and it unclear how much each (NOM or Cl^-) contributed to the reduction.

Gong et al. [2013] observed that the silver-loaded porous carbon spheres are eminent in removal Br^- from water. However, the Br^- adsorption can be impeded by several competitive species from water. They investigated the effect of competitive species, such as Cl^-, I^-, NO_3^-, SO_4^{2-} and humic acid on Br^- adsorption with their impact following the order: $I^- > SO_4^{2-} > NO_3^- > Cl^-$. They reported the feasible pH value for Br^- removal was between 4 and 7, and the optimal value was 5. But in the presence of competitive species, the impact of pH was minor, except for I^- anion. In addition, the performance of the silver-loaded porous carbon spheres improves with increasing temperature.

CHAPTER THREE

RESEARCH OBJECTIVES

The main motivation of this study is to evaluate the efficiency of SIAC as a potential adsorbent for bromide removal in various aqueous conditions. This study focuses on three main objectives:

The first objective was to determine the optimum silver impregnation protocols and assess the role of carbon characteristics (e.g., activated carbon characteristics, silver impregnation techniques and pre-oxidation conditions) to produce SIACs to remove Br^- from natural waters; and evaluate their effectiveness for Br^- removal.

The second objective was to evaluate the developed SIACs at typical water treatment conditions. This task involved mainly investigating the competing anions (e.g. Cl^-) and NOM and the background matrix effect in natural water samples (e.g. pH, TOC, SUVA, presence of alum during coagulation/flocculation, etc.)

The third objective was to evaluate the impact of selected SIAC for DBPs formation control (i.e., THMs control) in natural waters.

CHAPTER FOUR

MATERIALS AND METHODS

4.1 Materials

4.1.1 Activated Carbon

Four coal based GACs (HD3000 and 20B from Norit, Inc., F400 from Calgon Corp., WC800 from Standard Purification, Inc.) with different physicochemical properties (two mesoporous, HD3000, 20B; and two microporous, WC800, F400) were used in this study to produce SIACs in this study. In addition, two bituminous coal based commercially available SIACs with different silver contents, 1.05 wt. percent SIAC, (TOG-NDS-20*50, Calgon Corporation), and 4.03 wt. percent SIAC (Nusorb A 20*40, Nucon International, Inc.) were also used in this research, as received from the manufacturers.

Virgin GAC samples were crushed, sieved to 200-325 μm mesh size, and then washed with distilled and deionized water (DDW), dried at 90 ℃. The produced powdered activated carbon (PAC) from each GAC was stored in sealed containers. The selected physicochemical properties of the virgin activated carbons are summarized in Table 4.1.

Table 4.1 Virgin activated carbon characteristics

Carbon Name	Carbon Type	Specific Surface Area[a]	Total Pore Volume[b]	Pore Volume Distribution			Pore Volume Distribution			Oxygen Content	pH_{pzc}
		(m^2/g)	(cm^3/g)	(<2 nm)	(2<x<50 nm)	(>50 nm)	(%)	(%)	(%)	(%)	
20B	Coal	1748	1.42	0.33	0.83	0.26	23.0	58.5	18.5	0.9	5.4
F400	Coal	849.0	0.50	0.31	0.07	0.12	61.9	14.0	24.1	2.4	9.2
WC800	Coal	713.0	0.49	0.23	0.15	0.10	47.3	31.6	21.1	4.1	10.4
HD3000	Coal	642.0	0.77	0.11	0.45	0.22	13.9	58.0	28.1	4.4	6.9

[a] Specific surface area calculated with the Brunauer-Emmett-Teller (BET) model, [b] Total pore volume calculated from single point adsorption at P/P_0 = 0.99, [c] Pore volume in each pore size range obtained from the density functional theory (DFT) analysis.

4.1.2 Bromide Solution

The bromide stock solution (1000 mg/L) was prepared by dissolving sodium bromide (NaBr) salt (Sigma-Aldrich) of reagent grade (25.75 mg) in 20 mL deionized water and desired concentrations were obtained by diluting the bromide stock solution. Solutions containing other anions (NO_3^-, SO_4^{2-}, Cl^-) were prepared by mixing a known amount of the bromide stock solution and solutions with the specified anion.

4.1.3 NOM Solution and Natural Waters

The NOM isolate used in the study was collected from the influent of a drinking water treatment plant in South Carolina using a reverse osmosis and followed by resin fractionation, as described elsewhere [Song et al., 2009]. $SUVA_{254}$, defined as the ratio of UV absorbance at 254 nm divided by the dissolved organic carbon (DOC) concentration, has the units of L/mg-m, and it is a quantitative measurement of the aromatic content per unit concentration of organic carbon in water. Natural waters with high $SUVA_{254}$ values (e.g., more than 4.0 L/mg-m) have organic matter with relatively high contents of hydrophobic, aromatic, and high molecular weight components, whereas waters with $SUVA_{254} \leq 2.0$ L/mg-m contain mostly non-humic, hydrophilic and low molecular weight material [Karanfil et al., 2007].. Thus $SUVA_{254}$ was employed to characterize the NOM in this study. The DOC concentration was determined using a high-temperature catalytic combustion total organic carbon analyzer (Shimadzu TOC-V CSH). The UV_{254} absorbance was measured by a UV spectrophotometer (Varian Cary-50). The $SUVA_{254}$ value of NOM solution used in the experiments was around 4.0 L/mg-m. Using aquatic

NOM allows the assessment of the independent effects of NOM on bromide adsorption without the confounding effects of background anions and cations in natural waters. However, selected experiments were also performed with natural water samples collected from Charleston (CH), Myrtle Beach (MB), Bushypark Reservoir, Edisto River, Savannah River, Lake Hartwell (HW), and Broad River. The water characteristics are summarized in Table 4.2.

Table 4.2 Natural waters characteristics

	Br^- Concentration ppb	**Cl^- Concentration mg/L**	**SO_4^{2-} Concentration mg/L**	**NO_3^- Concentration mg/L**	**TOC mg/L**	**UV cm^{-1}**	**SUVA**
Charleston	81	15.3	6.0	0.08	11.8	0.201	1.7
Myrtle Beach	100	19.5	5.7	0.53	27.6	1.203	4.4
Bushi Park	79.9	29.5	5.7	0.3	4.4	0.170	3.9
Edisto River	33.2	37.9	7.7	0.51	5.0	0.260	5.2
Savanah River	197.5	40.4	10.7	1.04	3.3	0.110	3.3
Lake Hartwell	20.1	2.6	2.0	0.61	2.1	0.038	1.8
Broad River	95	14.3	6.3	0.35	5.4	0.160	3.0

4.2 Preparation of SIACs

4.2.1 Pre-oxidation

The virgin PACs (F400, HD3000, WC800 and 20B) were pre-oxidized by nitric acid (wet oxidation) with varying acidic strengths and heating temperatures prior to silver impregnation. Due to the fact that oxidation temperature, oxidant concentration and oxidation time are the three major factors that control the severity of carbon oxidation. The nitric acid oxidation experiments were performed at two different oxidation temperatures, and two nitric acid concentrations. Oxidation time was set to be 1 hour for carbon pre-oxidation.

High temperature oxidation with nitric acid were performed by adding 6 g of PAC sample in 150 mL concentrated nitric acid solutions (10 N or 15.7 N) and boiled (~160 ℃) for one hour on a hot plate. The temperature was raised until small bubbles could be seen in the solution, which is the sign of boiling. After 1 hour, the Erlenmeyer flask was removed from the hot plate and cooled to room temperature. The carbon samples were filtered and washed thoroughly with DDW several times. The pH of the supernatant was measured after each washing until it remained constant to make sure the extra acid was removed. Then, the PAC was dried at 90 ℃ and stored in a sealed container. Low temperature oxidation with nitric acid (15.7 N) was performed utilizing the same procedure but the nitric acid was heated to 90℃ instead of 160℃.

4.2.2 Silver Impregnation of Pre-oxidized Activated Carbons

The silver impregnation of pre-oxidized activated carbons was performed at three silver nitrate ($AgNO_3$) concentrations, 0.1 mol/L, 0.5 mol/L, 1.5 mol/L. Twenty mL $AgNO_3$ were added to 1 g of pre-oxidized PAC. The carbon slurry was stirred for two days at 150 rpm at room temperature. Then the carbon samples were filtered and washed several time with DDW, dried at 90℃ and stored in sealed containers. The four virgin GACs F400, HD3000, WC800 and 20B were modified by various peroxidation and silver impregnation techniques. The experiment matrix was summarized in Table 4.3.

Table 4.3 Experiment matrix of activated carbon modification

Carbon name	Pre-treatment	Impregnation
HD3000	None	0.5M $AgNO_3$
HD3000-05[a]	Oxidation by 10N HNO_3	0.5M $AgNO_3$
HD3000-05[b]	Oxidation by 15.7N HNO_3	0.5M $AgNO_3$
HD3000-05-low T	Low T oxidation by 15.7N HNO_3	0.5M $AgNO_3$
HD3000-05-high T	High T oxidation by 15.7N HNO_3	0.5M $AgNO_3$
WC800	None	None
WC800-01	Oxidation by 15.7N HNO_3	0.1M $AgNO_3$
WC800-05	Oxidation by 15.7N HNO_3	0.5M $AgNO_3$
WC800-15	Oxidation by 15.7N HNO_3	1.5M $AgNO_3$
WC800-05-low T	Low T oxidation by 15.7N HNO_3	0.5M $AgNO_3$
WC800-05-high T	High T oxidation by 15.7N HNO_3	0.5M $AgNO_3$
F400	None	None
F400-05	Oxidation by 15.7N HNO_3	0.5M $AgNO_3$
F400-05-low T	Low T oxidation by 15.7N HNO_3	0.5M AgNO3
F400-05-high T	High T oxidation by 15.7N HNO_3	0.5M AgNO3
20B	None	None
20B-05	Oxidation by 15.7N HNO_3	0.5M AgNO3

4.3 Characterization of Adsorbents

Nitrogen gas adsorption at 77K was performed with a physisorption analyzer (Micromeritics ASAP 2010) to determine the specific surface area (SSA), pore volume and pore size distribution of the adsorbents. The Brunauer-Emmett-Teller (BET) equation was used to calculate SSAs. The total pore volume was obtained from the adsorbed volume of nitrogen near the saturation point (P/P_0 = 0.99). Pore size distribution of adsorbents was determined from the nitrogen isotherms using the Density Functional Theory (DFT) model. Oxygen contents of the carbonaceous adsorbents were measured using a Flash Elemental Analyzer 1112 series (Thermo Electron Corporation). In addition, pH of the point of zero charge (pH_{PZC}) of adsorbents was determined was performed according to the method described by Muller et al., [1980] and Summers [1986]. NaCl (0.1M) solutions at pHs of 1, 3, 5, 7, 9, 11 were prepared using NaOH and HCl. One hundred mg of each carbon were placed in a 25 mL bottle, and the bottles were filled with solutions to prevent headspace development. Bottles were prepared in triplicate for each material at each pH value. The point of zero charge (PZC) was found by showing initial pH versus final pH, as the PZC exists at the point where there is no change in pH after contact with the carbon. The technique is a selective neutralization of surface acidic groups by varying strength of bases and basic groups by a strong acid and is described by Karanfil [1995]. The silver contents of SIAC were determined through digestion followed by inductively couple plasma mass spectroscopy (ICP-MS) analysis.

4.4 Adsorption Experiments

Carbon doses of 50 and 25 mg/L were used for the commercial and lab modified SIACs experiments, respectively. Four types of experiments were conducted at room temperature (20±3 ℃),

(1). Constant carbon dose aqueous phase kinetic experiments:

Kinetic experiments in DDW were conducted in completely mixed batch reactors (CMBRs of 50 mL plastic bottles). Br^- stock solution was prepared from a sodium bromide stock solution. Fifty mL of 250 ppb Br^- stock solutions were added in 50 mL polypropylene tubes (i.e., CMBRs) which contained a constant SIAC dose of 50 mg/L. The CMBRs were placed in a rotary tumbler for 1, 2, 4, 8, 12, 24, and 48 hours contact time. Preliminary rate experiments showed 48 hours to be satisfactory for reaching equilibrium. After the target contact time, the sorbents were separated from solution by filtration. The filtrate was analyzed by Ion Chromatography (IC) to obtain the residual bromide concentration in the solution after SIAC adsorption.

Kinetic experiments in natural waters were conducted using the same procedure as described in DDW. The natural waters were spiked with 300 ppb bromide initial concentration, along with background ions (Cl^-, SO_4^{2-}, NO_3^-, etc.) and natural organic matters (NOM) depending on the goal of the experiments. The kinetic experiments were conducted for 1, 2, 4, 8, 12, 24 and 48 hours contact time, the experiment matrix is shown in Table 4.4.

Table 4.4 Experiment matrix for Br^- adsorption kinetics

Adsorbent	Contact time hours	Water solution
4.03% SIAC	1	DDW
4.03% SIAC	2	DDW
4.03% SIAC	4	DDW
4.03% SIAC	8	DDW
4.03% SIAC	12	DDW
4.03% SIAC	24	DDW
4.03% SIAC	48	DDW
4.03% SIAC	1	Broad River
4.03% SIAC	2	Broad River
4.03% SIAC	4	Broad River
4.03% SIAC	8	Broad River
4.03% SIAC	12	Broad River
4.03% SIAC	24	Broad River
4.03% SIAC	48	Broad River

(2). Constant carbon dose aqueous phase 4-hour adsorption experiments:

For selected natural water experiments, adsorption experiments were conducted with WC800, HD3000, 20B and F400 SIACs for 4 hours contact time to mimic actual water treatment conditions in drinking water treatment plants. From preliminary experiment, the carbon dose for bromide removal was selected to be 25 mg/L. The initial bromide concentration in the aqueous solution was spiked to ~300 ppb in all background water conditions (DDW, NOM solution, Cl^- spiked solution, or natural source waters). The experimental matrix for these experiments is summarized in Table 4.5.

Table 4.5 Experiment matrix for four-hour Br^- removal in various water conditions

Background water condition	WC800 SIAC	HD3000 SIAC	20B SIAC	F400 SIAC
DDW	√	√	√	√
NOM	√	√	√	√
NOM+40Cl		√	√	√
HW	√	√	√	√
HW+40Cl	√	√	√	√
MB	√	√	√	√
MB+40Cl	√	√	√	√
Broad River	√	√	√	√
Charleston	√			
Bushypark	√			
Edisto	√			
Savannah	√			

√: a completed Br adsorption experiment with the certain carbon.
NOM: 2.5 mg/L NOM solution; NOM+40Cl: 2.5 mg/L NOM+ 40 mg/L Cl; HW: lake Hartwell water; HW+40Cl: lake Hartwell water +40 mg/L; MB: Myrtle Beach water; MB +40Cl: Myrtle Beach water+ 40 mg/L Cl.

Four-hour Br^- adsorption experiments in DDW were conducted in completely mixed batch reactors (CMBRs, i.e., 50 mL plastic bottles). The target bromide concentration (i.e., 300 μg/L) in solution was attained with a spike from a sodium bromide stock solution. Four-hour bromide adsorption experiments in natural waters were conducted the same way as in DDW water.

(3) Jar test

In these experiments, 4.03% (silver %) commercial SIAC was used.

Silver impregnated activated carbon was added to water before coagulation/flocculation in water treatment. For the jar test experiment, the coagulant (alum) dose was set at 30 mg/L, a natural water (from Broad river) was used. The SIAC was the 4.03% silver content carbon, and the F400 carbon with no silver was used in a

separate experiment. F400 was selected as the closest carbon for the production of 4.03% SIAC. The 4.03% commercial SIAC carbon dose were selected as 10 mg/L, 25 mg/L, 50 mg/L; and the initial pH was 7.28, and decreased to 6.48 after 30 mg/L alum was added. The pH remained unchanged during the rapid and slow mixing. The rapid mixing was conducted at 200 rpm for one minute followed by slow mixing at 25 rpm for 20 min, and then two hours of settling time was provided. Eight jars were used, to investigate the bromide removal efficiency of the following adsorbents: 30 mg/L alum only; 50 mg/L F400 PAC; various dose SIAC with no alum added (10 mg/L, 25 mg/L, 50 mg/L carbon dose); various dose SIAC with 30 mg/L alum added (10 mg/L, 25 mg/L, 50 mg/L carbon dose), as shown in Table 4.6.

Table 4.6 Experiment matrix for Br^- removal in jar test

Adsorbent	Carbon dose mg/L	Alum dose mg/L
Alum	0	30
F400 virgin PAC	50	0
4.03% SIAC	10	0
4.03% SIAC	25	0
4.03% SIAC	50	0
4.03% SIAC	10	30
4.03% SIAC	25	30
4.03% SIAC	50	30

(4) THM formation control experiment

The WC800-05 low T SIAC dose was 25 mg/L, and the Br^- spike concentration was 290 ppb. Carbon adsorption experiments were conducted in 250 mL plastic bottles with caps. The SIAC retention time was four hours. For the chlorine demand test after adsorption, HOCl was used to achieve >0.4 mg/L residual after one day contact time and phosphate buffer was added to maintain the pH about ~7.8. The chlorinated samples were

analyzed by GC (gas chromatography) to measure THM concentrations. WC800 low temp ox SIAC, with 3.4% silver content and 764.5 m2/g BET surface area, was used for this set of experiments in three water conditions: NOM+ 40Cl (2.5 mg/L TOC, 40 mg/L Cl^-), HW raw (2.3 mg/L TOC, 2.6 mg/L Cl^-), and HW+ 40Cl (2.3 mg/L TOC, 40 mg/L Cl^-). The experiment matrix is presented in Table 4.7.

Table 4.7 Experimental matrix for Br^- removal effect on THM control

	Demand test	THM formation test	UV	TOC	IC
NOM+40Cl	√	√	√	√	√
NOM+40Cl+300Br	√	√	√	√	√
NOM+40Cl+300Br+25mg/LSIAC		√	√	√	√
HW	√	√	√	√	√
HW+300Br	√	√	√	√	√
HW+300Br+25mg/L SIAC		√	√	√	√
HW+40Cl	√	√	√	√	√
HW+40Cl+300Br	√	√	√	√	√
HW+40Cl+300Br+25mg/L SIAC		√	√	√	√

√: a completed experiment

4.5 Analytical Methods

The analytical methods utilized in this study and detection limits are summarized in Table 4.8.

Table 4.8 Analytical methods and minimum detection levels

Parameter	Measurement Method	Equipment	Minimum Detection Levels	Unit
DOC & TOC	SM 5310B	TOC-VCSH, Shimadzu Corp., Japan	0.1	(mg/L)
UV_{254} Absorbance	SM 5910	Cary 50, Varian Inc., USA	± 0.001	(abs)
Br^-,NO_3^-,NO_2^-,SO_4^{2-}	USEPA Method 300	ICS-2100, Dionex Corp.	Br^-: 10, NO_3^-: 15, NO_2^-: 20, SO_4^{2-}: 20	(μg/L)
pH	SM 4500-H^+	420A, Orion Corp,USA	±0.01	
THM_4	USEPA Method 551.1	Agilent 6890 or 6850 μ-ECD	1	(μg/L)
Free/Combined Chlorine	SM 4500-Cl F	NA	0.1-0.15	(mg/L)

NA: not applicable

DOC/TOC was measured using a Shimazu TOC-V_{CHS} high temperature combustion analyzer equipped with TNM-1 module. UV absorbance at 254 nm (UV_{254}) was determined using a 1 cm quartz cell on a Cary 300 UV-Vis spectrophotometer. Specific UV absorbance ($SUVA_{254}$) was calculated by dividing DOC concentration by the UV_{254}. Anions were determined using a Dionex ICS 2100 ion chromatograph and following the USEPA Method 300.1. The silver content of SIACs was measured on an inductively coupled plasma (ICP) atomic emission spectroscopy instrument.

All the THM measurements were carried out in duplicate. Four THM species were extracted following USEPA Method 551.1with some modifications. The extracts were analyzed using a gas chromatograph with an electron capture detector (GC/ECD). The details of the analytical methods were previously reported elsewhere [Hong et al., 2009; Hu et al., 2010b].

CHAPTER 5

RESULTS AND DISCUSSION

5.1 The Effect of Silver Impregnation on Carbon Characteristics

5.1.1 The Effect of Pre-oxidation

Nitric acid oxidation creates various oxygen-containing functionalities on the carbon surface, particularly strong (e.g., carboxylic) and intermediate (e.g., lactone and lactol) acidic groups [Vinke et al., 1994]. The objective of producing oxidized carbon in this study was to prepare proper precursors for silver impregnation, by producing sufficient number of exchangeable protons of oxygenated groups with Ag^+. In addition, the created negatively charged oxygenated groups made the carbon surface more attractive for the Ag^+ to attach to.

Pre-oxidation alters the physicochemical properties (e.g. SSA and oxygen content) of ACs. The severity of wet oxidation (by HNO_3) may be adjusted or controlled by a combination of oxidant concentration, oxidation time and oxidation temperature [Wan mohd et al., 2009]. The effects of oxidant concentration and oxidation temperature are described below.

5.1.1.1 HNO_3 Concentration

Two PACs (HD3000 and WC800) were used to investigate the HNO_3 concentration effect. The carbon oxygen content and specific surface areas (SSAs) of virgin and oxidized PACs were presented in Table 5.1.

Table 5.1 Carbon oxygen content and SSA before and after pre-oxidation with different HNO_3 concentrations

Sample Name	**Oxygen Content %**	**SSA m^2/g**
HD 3000 raw PAC	4.4	642.0
HD3000 pre-ox PAC by $10HNO_3$	18.6	528.4
HD3000 pre-ox PAC by $15.7HNO_3$	19.1	524.8
WC 800 raw PAC	4.1	644.3
WC800 pre-ox PAC by $10HNO_3$	10.9	569.3
WC800 pre-ox PAC by $15.7HNO_3$	15.1	438.6

Two major observations were made: First, both HD3000 and WC800 showed elevated oxygen content and decreased SSA after oxidation; and the 15.7N acid pre-oxidation resulted in higher oxygen content than the 10N pre-oxidation. Second, a larger SSA decrease was observed when more concentrated nitric acid (15.7 N) was used. Third, WC800 AC is microporous, compared to HD3000 (mesoprous), higher degree of SSA deduction was observed, there was a more decrease in SSA for microporous AC than mesoporous AC after pre-oxidation by 15.7 HNO_3. Previous researches have also reported a decrease in surface area and pore volume when microporous AC was oxidized by HNO_3. The decrease was attributed to one or a combination of reasons such as pore blockage by oxygen surface groups (produced by acidic treatment); electrostatic repulsion of surface probe molecules (nitrogen) and wall erosion or destruction of micropore walls by liquid oxidants [Gorgulho et al., 2008; El-Sayed et al., 2001; Szymanski et al., 2004; Strelko et al., 2002].

5.1.1.2. Oxidation Temperature

HD3000, WC800 and F400 were used to investigate the oxidation temperature effect. Both low temperature and high temperature oxidation were applied to the same virgin PACs. The carbon oxygen content and SSA results are presented in Table 5.2.

Table 5.2 Carbon oxygen content and SSA before and after pre-oxidation with different oxidation temperatures

Sample Name	Oxygen Content %	SSA m^2/g
HD 3000 raw PAC	4.4	642.0
HD 3000 low T ox PAC by 15.7HNO_3	15.9	530.1
HD 3000 high T ox PAC by 15.7HNO_3	19.1	373.6
WC 800 raw PAC	4.1	644.3
WC800 low T ox PAC by 15.7HNO_3	15.1	624.5
WC800 high T ox PAC by 15.7HNO_3	18.9	367.9
F400 raw PAC	2.4	978.0
F400 low T ox PAC by 15.7HNO_3	15.6	905.3
F400 high T ox PAC by 15.7HNO_3	19.1	472.3

low T: ~90℃; high T: ~160℃

Compared to the virgin PACs, an increase of oxygen content and a decrease of SSA were observed after oxidation. The temperature effect was considerable, higher oxygen content and larger decrease in surface area was observed at higher oxidation (About 270- 500 m^2/g SSA decrease for PAC pre-oxidation at 160℃ compared to 20-100 m^2/g SSA decrease at 90℃). The changes can be attributed to the high temperature oxidation causing more wall erosion and collapse of carbon pores [Barton et al., 1997].

In conclusion, for the PACs used in this study, relatively higher oxygen content (an indication of the presence of new oxygen-containing functionalities) and smaller SSA were observed after oxidation. The severity of oxidation was influenced by both of the tested two factors, i.e. oxidant concentration (10 N and 15.7 N HNO_3) and oxidation

temperature (160 ℃ and 90 ℃), among which the oxidation temperature was more influential on PAC characteristics.

5.1.2 The Effect of Silver Impregnation

The virgin materials (Table 4.1) were impregnated in our lab following pre-oxidation. The SSA, oxygen content and silver content of SIACs are presented in Table 5.3. The SSA of ACs ranged between ~263 – 1748 m^2/g, the silver content ranged between 1.1 – 12.3% and the oxygen content ranged between ~1 – 20%. There was no correlation between the oxygen and silver content of the PACs. There was a negative correlation (R^2 = 0.8) between silver content and SSA (see Figure 5.1). The decrease in SSA with increasing oxygen content was attributed to depletion and blockage of pores as a result of silver impregnation of PACs.

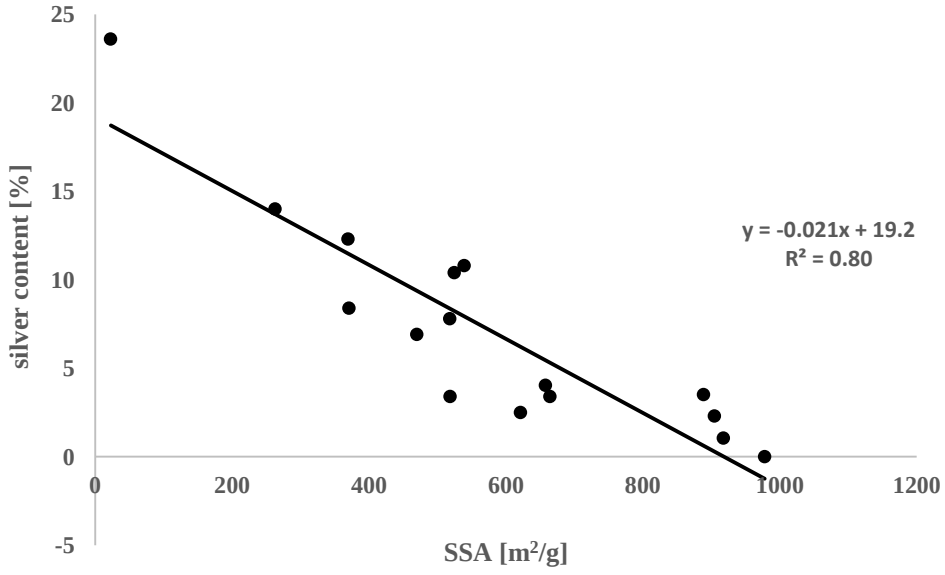

Figure 5.1 Correlation of silver content and SSAs of SIACs.

Table 5.3 Activated carbon characterization before and after silver impregnation

Sample Name	Base carbon	Oxygen	SSA	Silver Content
		%	m^2/g	%
HD 3000 raw PAC	Lignite coal	4.4	642	-
HD 3000 raw SIAC by 0.5M $AgNO_3$		4.3	635.3	2.1
HD 3000 10ox SIAC by 0.5M $AgNO_3$		18.9	528.4	7.8
HD 3000 15.7ox SIAC by 0.5M $AgNO_3$		19.1	524.8	10.4
HD 3000 low temp ox SIAC by 0.5M $AgNO_3$		15.6	524.7	2.5
HD 3000 high temp ox SIAC by 0.5M $AgNO_3$		18.9	370.8	8.4
WC 800 raw PAC	Coal	4.1	644.3	-
WC 800 raw SIAC by 1.5M $AgNO_3$		3.9	621.6	2.5
WC 800 15.7ox SIAC by 1.5M $AgNO_3$		17.4	262.7	14
WC 800 15.7ox SIAC by 0.1M $AgNO_3$		13.7	518.6	3.4
WC 800 15.7ox SIAC by 0.5M $AgNO_3$		14.6	539.1	10.8
WC 800 low temp ox SIAC by 0.5M $AgNO_3$		14.5	664.5	3.4
WC 800 high temp ox SIAC by 0.5M $AgNO_3$		18.5	369.7	12.3
20 B raw PAC	Coal	0.93	1748	-
20 B 15.7ox SIAC by 0.5M $AgNO_3$		19.6	1681	3.6
F400 raw PAC	Bituminous coal	2.38	978	-
F 400 low temp ox SIAC by 0.5M $AgNO_3$		15.0	904.8	2.3
F400 high temp ox SIAC by 0.5M $AgNO_3$		18.7	469.8	6.9
1.05% commercial SIAC	Bituminous coal	N/A	918	1.1
4.03% commercial SIAC	Bituminous coal	N/A	658	4.0

*underlined values are the maximum and minimum values of each column

5.2 The Effect of Silver Impregnation on Br^- Removal

5.2.1 The Effect of Pre-Oxidation

HD3000 virgin PACs were treated as follows: (i). no pre-oxidation, impregnated with 0.5M $AgNO_3$ solution, labeled as HD3000-05 raw SIAC; (ii). Pre-oxidized by 10N HNO_3, then impregnated with 0.5M $AgNO_3$, labeled as 10 ox HD3000-05 SIAC; (iii). pre-oxidized by 15.7N HNO_3, then impregnated by 0.5M $AgNO_3$, labeled as 15.7 ox

HD3000-05 SIAC (the oxidation temperature for (ii) and (iii) was 160 ℃). The experimental results are presented in Figure 5.2.

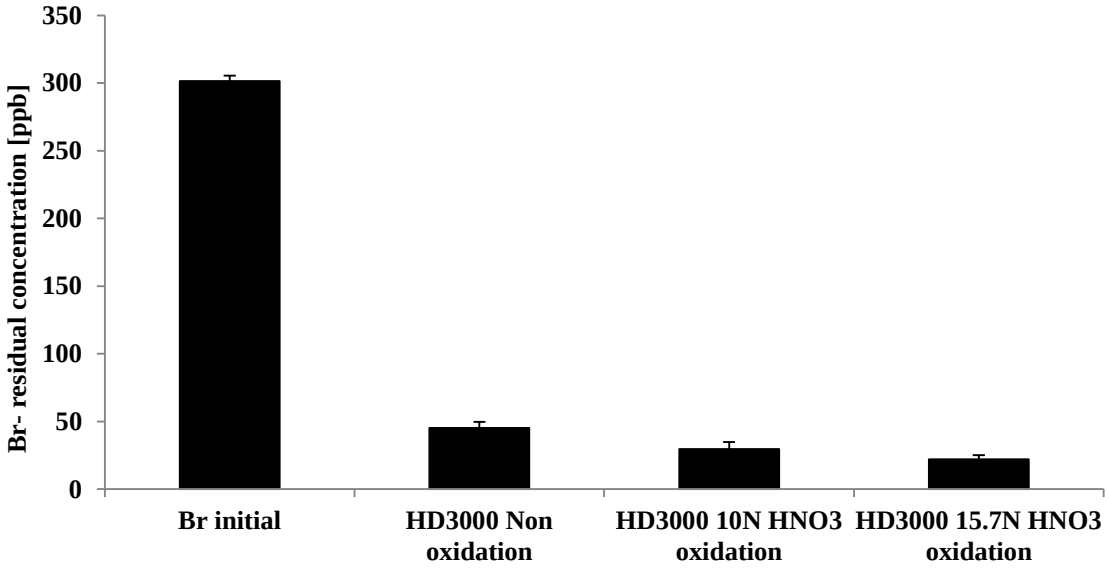

Figure 5.2 Pre-oxidation effect on Br^- removal by SIACs in DDW. All Br^- concentrations reported as mean ± percentage error obtained from duplicates.

All the SIACs effectively removed Br^- from DDW regardless of pre-oxidation treatment with removals of ~85 to 93%, however, stronger pre-oxidation treatment caused slightly better removal. The Br^- removal was in the order of 15.7 N ox HD3000-05 > 10 N ox HD3000-05 > HD3000-05-raw. The 15.7 N ox HD3000-05 showed ~25 ppb more Br^- removal than the HD3000-05-raw SIAC. The pre-oxidation of PACs showed positive effect on Br^- uptake by SIACs over no pre-oxidation. In addition, higher Br^- uptake by SIAC was observed by utilizing 15.7N HNO_3 as the oxidant. In a previous study by Cheng [2006], 15.7N HNO_3 was also selected as the oxidant for pre-oxidation of activated carbon, followed by iron impregnation.

5.2.2 The Effect of Silver Impregnation

To investigate the silver impregnation effect on Br^- removal by SIACs, Br^- adsorption experiments were conducted at the same pre-oxidation condition with WC800 in DDW. WC800 virgin PAC was pre-oxidized by 15.7N HNO_3 for all impregnation conditions, treated with silver and labeled as follows: (i). no silver impregnation, WC800-0 ox PAC; (ii). impregnated with 0.1M $AgNO_3$ solution, WC800-01 ox SIAC; (iii). impregnated with 0.5M $AgNO_3$, WC800-05 ox SIAC. (iv)Pre-oxidized by 15.7N HNO_3, then impregnated by 1.5M $AgNO_3$, WC800-15 ox SIAC (the oxidation temperature for (i), (ii), (iii) were 160 ℃); The experimental results are presented in Figure 5.3.

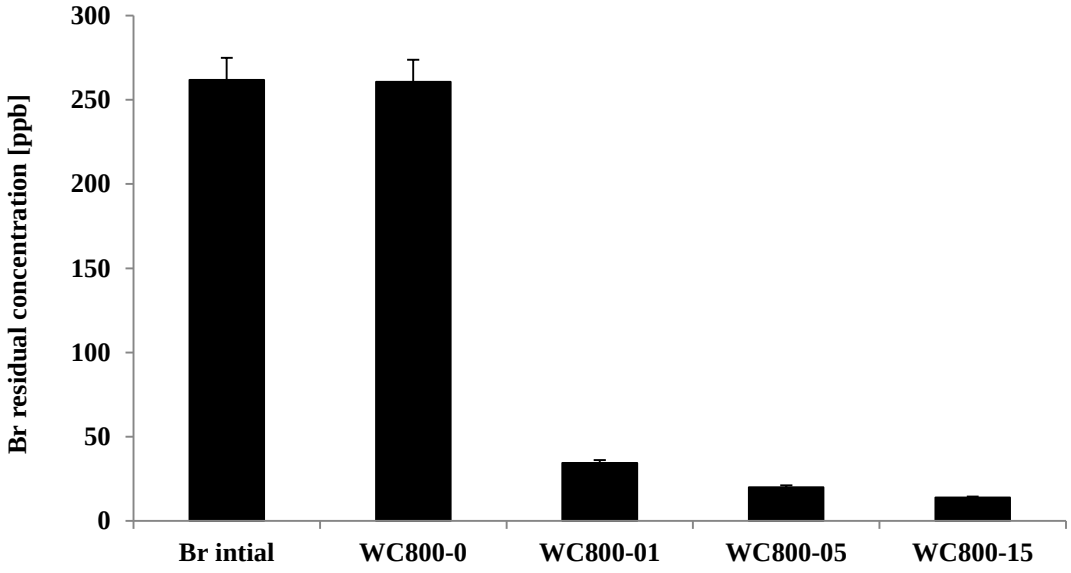

Figure 5.3 Silver impregnation effect on Br^- removal in DDW (01, 05, 15 shows the concentration of silver salt for impregnation was 0.1, 0.5, 1.5M; contact time 4 hours). All Br^- concentrations reported as mean ± percentage error obtained from duplicates.

Some major observations from the Br^- adsorption experiments were as follow: First, the PACs with silver impregnation showed up to 87% - 95% Br^- removal, by

contrast there was very little Br^- uptake by the oxidized WC800 PAC with no silver impregnation, the silver impregnation was the predominant factor for Br- removal, the Br^- was removed because of the silver species present on the SIAC surface. Second, Br^- removal order in DDW from high to low is WC800-15 ox > WC800-05 ox > WC800-01 ox> WC800-0. Larger amount of Br^- was removed by SIACs impregnated by higher concentration of silver salt. Third, ACs impregnated by highly concentrated (1.5M) $AgNO_3$ did not show considerably higher Br^- uptake than the others. Furthermore, the 0.5M $AgNO_3$ impregnation can reach the same level of bromide uptake (~6 ppb difference between WC800-05 and WC800-15). Therefore, due to the economic feasibility, 0.5M would be more appropriate $AgNO_3$ concentration for silver impregnation process.

5.2.3. The Effect of SIAC Characteristics

Four SIACs were investigated to understand the effect of carbon characterization on Br^- removal. In this study, Br^- adsorption experiments were conducted with 20B-05, F400-05, HD3000-05, and WC800-05 SIACs. Silver impregnation greatly enabled the SIAC to remove Br^- from aqueous solutions. From preliminary experiments, the virgin activated carbons showed no Br^- removal from DDW, while the SIACS showed up to 95% percent of Br^- removal in DDW spiked with ~300 ppb Br^- at a 25 mg/L carbon dose'.

The Br^- adsorption experiment results are presented in Figure 5.4 and 5.5. The Br^- residual concentrations after SIACs adsorption are presented in Figure 5.4, and the Br^- removal capacity (Q_e) is shown in Figure 5.5. First, the SSAs of the SIACs follow the

order of 20B (1680 m^2/g)> F400 (889 m^2/g) > WC800 (539 m^2/g) > HD3000 (525 m^2/g). The silver content of the SIACs are: HD 3000 (10.4%) > WC800 (10.3%) > 20B (3.6%) > F400 (3.5%). The Br^- removal by SIACs from high to low is: 20B-05 > F400-05 > HD3000-05 and WC800-05. There was no correlation between the silver content and Br^- uptake in DDW. Second, it was observed that the SIACs with higher SSAs showed better Br^- removal in DDW. The enhanced removal was attributed to the higher SSAs which provide more active adsorption sites on the SIAC surface, and it is easier for the free Br^- to precipitate with the Ag^+. Therefore, maintaining a high SSA during the pre-oxidation and silver impregnation process is of great importance to get good Br^- removal.

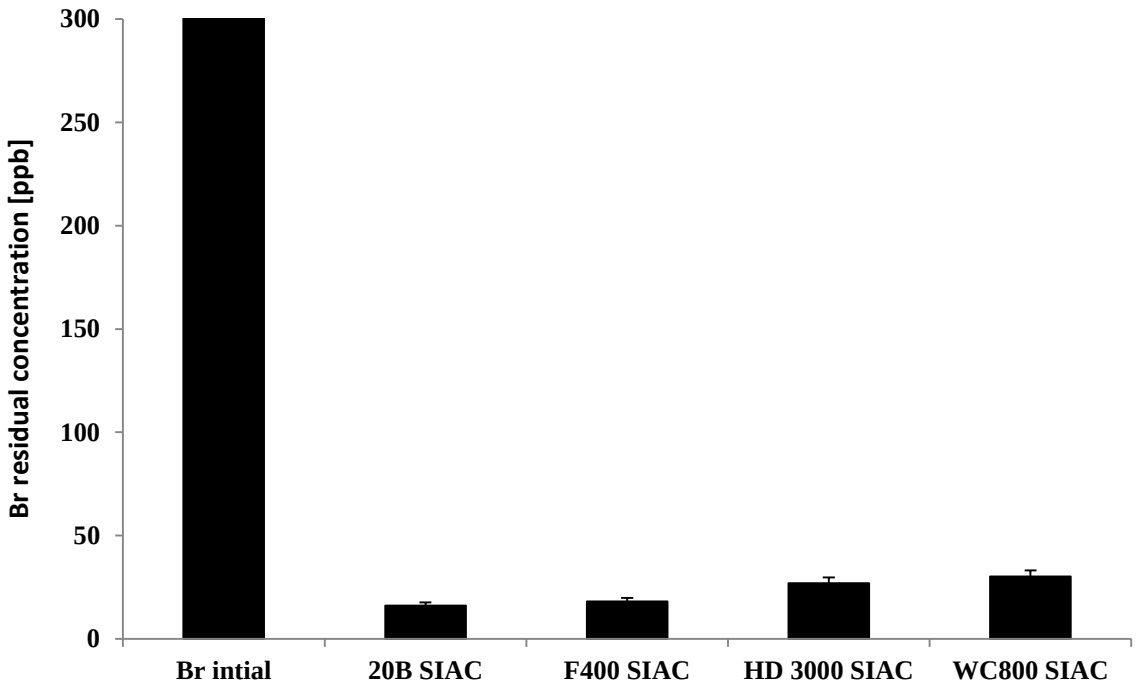

Figure 5.4 Br^- adsorption experiments in DDW by different SIACs (carbon dose: 25mg/L). All Br^- concentrations reported as mean ± percentage error obtained from duplicates.

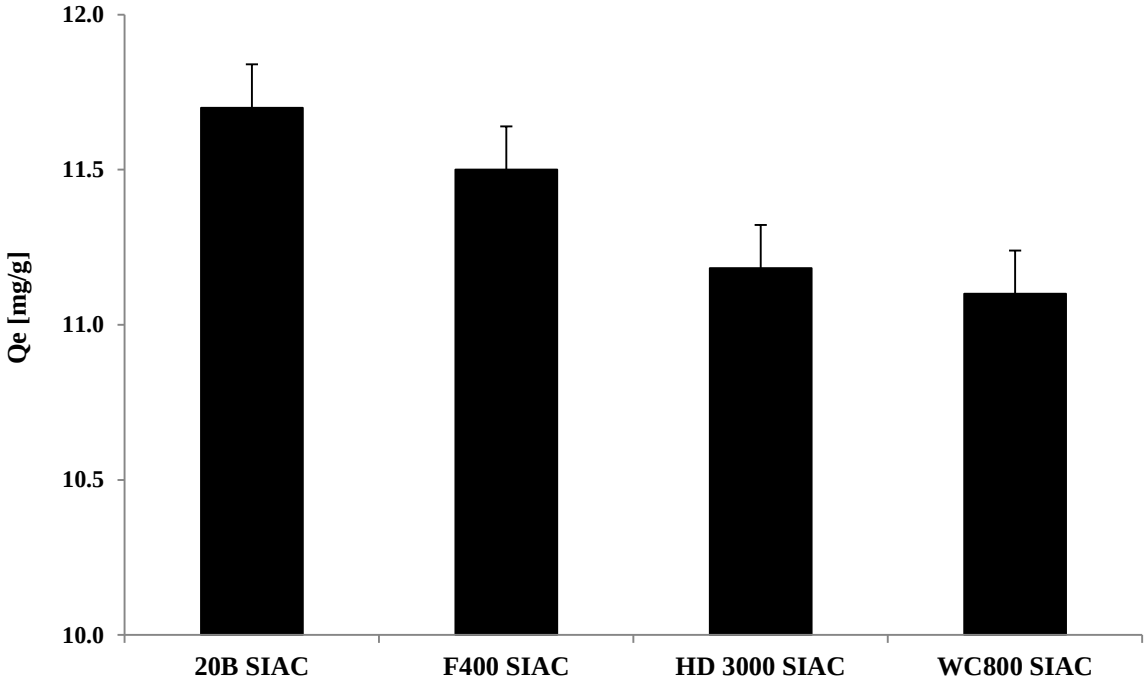

Figure 5.5 Br^- removal capacity by different SIACs in DDW (Q_e). All Br^- concentrations reported as mean ± percentage error obtained from duplicates.

Third, the silver content of SIACs had no correlation with the Br^- adsorption; up to 10.5% silver of WC800-05 SIAC had similar or even less Br^- adsorption than the 3.5% silver percent 20B-05 SIAC. The lack of correlation can be attributed to the fact that higher surface area of the activated carbon was also important factors for Br^- removal. In addition, according to stoichiometry, to remove 300 ppb Br^- in water (at 25 mg/L SIAC dose), the least silver percentage on SIAC is only ~ 1.62%.

$$Ag^+ + Br^- \rightarrow AgBr_{(s)},\ K_{sp} = 5.2 \times 10^{-13} \qquad \text{(Reaction 2)}$$

In the impregnation process, the $AgNO_3$ concentrations were 0.1M, 0.5M, and 1.5M, each concentration was abundant compared to the theoretical value (1.62%), and the achieved silver contents of the SIACs were all above 1.62%. Therefore the higher

silver content does not necessarily result in better Br^- removal. However, if in the presence of competing ions or NOMs, the higher silver content on the carbon surface can increase the chances for the Br^- to react and precipitate. In addition, the economic feasibility of the SIACs being used in drinking water treatment plants should be also considered.

5.3 The Effect of Background Water Chemistry on Br^- Removal by SIACs

Natural waters have varying concentrations of anions (e.g. Cl^-, SO_4^{2-}, NO^{3-}, PO_4^{3-}, etc) that may impede the Br^- removal by competing for sorption sites. The low silver salt solubility constant ($K_{sp}AgCl= 2.8*10^{-10}$) and high concentration in natural waters, makes Cl^- an effective competitor with Br^-. Sanchez-polo et al. [2006] reported that the Br^- removal capacity of Ag-coated aerogels in the presence of Cl^- was decreased ~35% indicating a competition for sorption sites. While they also observed NOM molecules in natural water block pores or compete for Ag-coated surface sites, they did not distinguish the respective effects of Cl^- and NOM since the selected natural water had both constituents. It was unclear how much each contributed to the reduction.

Removal performance experiments were undertaken to investigate the potential competitive factors (Cl^-, NOM, etc.) at environmentally relevant concentrations. These experiments were conducted at four hours and the SIACs were the 325μm mesh size, likely to be used in water treatment plants.

5.3.1 The Effect of Chloride

Preliminary experimental results showed no significant competition between Br^- and soluble ions i.e., NO_3^-/SO_4^{2-}. Therefore, the removal performance experiments were undertaken to investigate the effect of the potentially competitive soluble ion at its environmentally relevant concentrations Cl^- (10mg/L, 40mg/L), at pH 6 to 7 which encompass the typical pH of water treatment.

To investigate the Cl^- dose effect on Br^- adsorption, 1 mg/L, 10 mg/L, 50 mg/L, and 200 mg/L Cl^- dosages were selected. The experiment results are presented in Figure 5.6.

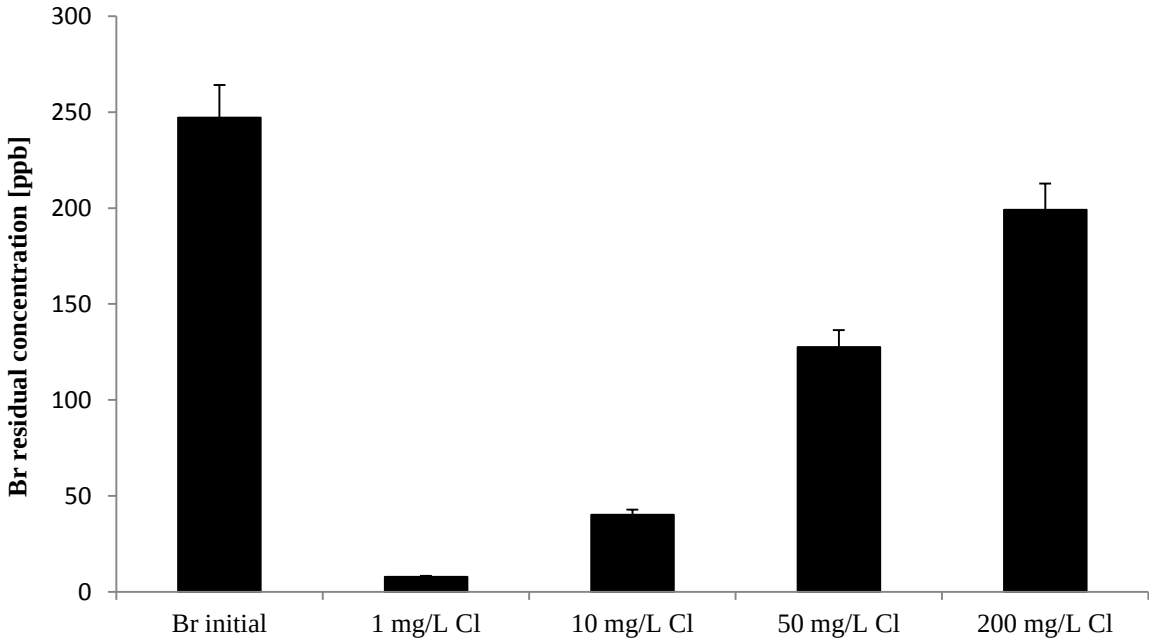

Figure 5.6 Cl^- dose effect on Br^- removal by 4.03% SIAC in DDW (carbon dose: 50 mg/L). All Br^- concentrations reported as mean ± percentage error obtained from duplicates.

It is evident that as the Cl^- dose increases, the Br^- removal decreases. The Br^- removal was 83.5% at 10 mg/L Cl^- dose; in the presence of 50 mg/L Cl^-, the Br^- removal decreased to ~38.1%; when the Cl^- dose increased to 200 mg/L, the overall Br^- removal

dramatically dropped to only ~7%. The large decrease of Br^- removal at increasing Cl^- dose showed the high concentration Cl^- in water was a strong competitor of Br^-. Possible postulation was that the Cl^- and Br^- compete to reach to the silver located in the carbon pores and form silver halide precipitate ($AgCl_{(s)}$ and $AgBr_{(s)}$). In addition, although the $AgCl_{(s)}$ solubility is higher than $AgBr_{(s)}$ (Ksp AgCl= 2.8×10^{-10}, Ksp AgBr= 5.2×10^{-13}) the Cl^- has much higher concentration (~33- 670 times) than the Br^-. The Cl^- competition results in the lower amount removal of Br^-.

Another important finding is that the Cl^- to Br^- ratio plays a role in the adsorption of Br^- by SIACs. Chloride is a common anion in nature, with the Cl^- to Br^- ratio typically ranging between 50- 1000 in surface waters, depending on the source, precipitation rates and human influences (e.g., road salt). Higher Cl^-: Br^- ratios are caused by urban runoff containing halite that is used as an anti-icing agent; the lower ratios indicate presence of anthropogenic bromide sources. In natural waters, the Cl^-: Br^-ratio remains a relatively constant level. But at areas impact by anthropogenic (Br^-) input, for example, bromide salts are used in combustion for mercury control and in the biocides used in cooling water at power plants. The presence of extremely high Br^- levels (1000- 10000 mg/L) have also been detected in the process/flow-back waters used in hydraulic fracturing operations. It is not always possible to isolate and eliminate the Br^- inputs from multiple sources in a watershed. I also observed a very low Cl^-: Br^- ratio (<50) in the Broad River, SC, which is located downstream of a power plant. When the Cl^- is no longer the dominant species

in water solution, i.e. at low Cl^-: Br^- ratio (< 50), the Cl^- competition is inhibited, and the adsorption of Br^- by SIAC can largely increase.

To investigate the Cl^-: Br^- ratio effect, Br^- adsorption experiments by WC800-05 SIAC were undertaken at two different Br^-initial concentrations (750 ppb and 290 ppb) in Lake Hartwell (HW) water (Cl^- initial concentration 2.6 mg/L). The results are presented in Figure 5.7.

First, as shown in Figure 5.7a, for HW raw water (Br^- initial was 750μg/L, Cl^-: Br^- ratio was 3.5), the Br^- removal percentage was up to 70%. In Figure 5.7b, Br^- initial was 290 μg/L (the Cl^-: Br^- ratio was 9), the Br^- removal percentage was 67%, low Cl^-: Br^- ratios resulted in large Br^- adsorption. Second, for NOM+40Cl water, the Cl^-: Br^- ratio was 55 (40 mg/L Cl^- and 750μg/L Br^-), the Br^- removal percentage was 61%. However, when the Cl^-: Br^- ratio increased to140 as shown in Figure 5.7b (40 mg/L Cl^- and 290μg/L Br^-), the Br^- removal percentage decreased to 52%. Third, for HW+40Cl water, 58% of Br^- was removed at a Cl^-: Br^- ratio of 55 (see Figure 5.7a), but as the Cl^-: Br^- ratio increased to 140, the Br^- removal percentage largely decreased to only 39% (see Figure 5.7b). In conclusion, the Cl^-: Br^- ratio in water played an important role on the Br^- removal by SIACs, the amount of Br^- removal decreases as the Cl^-: Br^- ratio of the water increase.

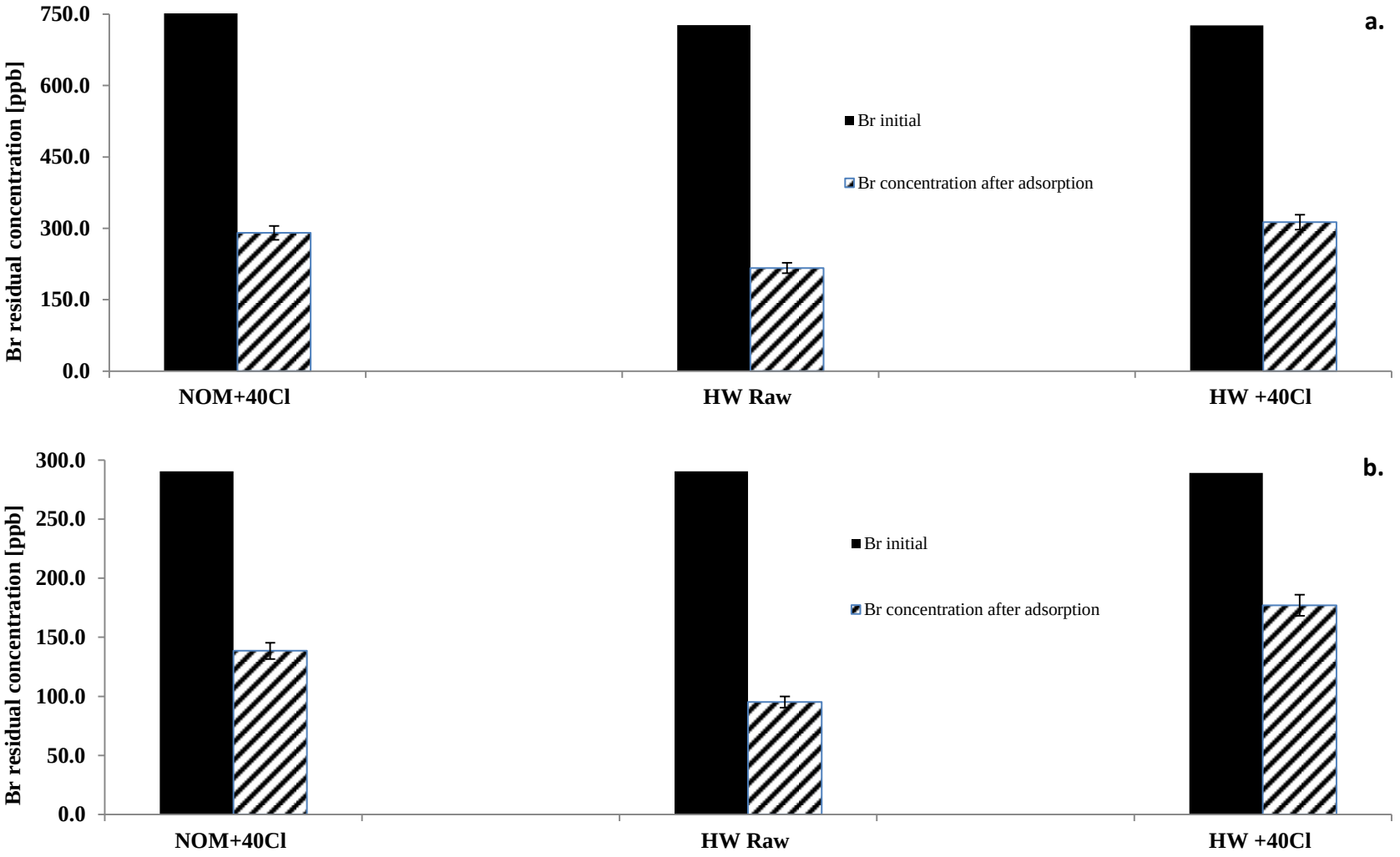

Figure 5.7 a. Br^- removal by WC800 low T SIAC in NOM and HW (Br^- initial: ~750 ppb); b. Br^- removal experiment by WC800 low T ox SIAC in NON (2.5 mg/L) and HW (Br^- initial: ~290 ppb). All Br^- concentrations reported as mean ± percentage error obtained from duplicates.

5.3.2 The Effect of NOM

Natural organic matter (NOM) is the organic material present in surface or ground waters. NOM includes both humic and non-humic fractions. The humic fraction includes high molecular weight organic molecules such as humic and fulvic acids. These substances plus tannic acid are the major fraction of dissolved organic matter (DOM) in water. These substances are oxidized very slowly and their solubility in water may vary with pH. NOM substances are potential precursor for DBPs (disinfection byproducts). The dissolved fraction of NOM may not be fully removed using conventional water treatment practices and has been shown to produce by-products such as trihalomethane during disinfection.

Activated carbon is a heterogeneous and porous adsorbent with very high capacity for adsorbing high quantities of contaminants from water. The ability of activated carbon to adsorb large quantities of materials is directly related to its porous structure and extraordinary large surface area [Summers et al., 1988; Baker et al., 1992]. The impregnation of PAC enables the SIAC to selectively remove Br^- (and I^- and other halogen ions) from aqueous solution. However, the PAC can still non-selectively adsorb substances such as NOM. Therefore, the NOM competes with the Br^- in water for the adsorption site on the SIAC surface; the large molecule of NOMs could even block the carbon pores and prevent the Br^- from reaching into the pores, and result in less Br^- removal by the SIACs.

In order to investigate the NOM competition with Br^- in water, several experiments were conducted with the SIACs; the NOM isolates were collected from the influent of a drinking water treatment plant in South Carolina using a reverse osmosis and followed by resin fractionation, as introduced in previous chapter. The NOM effect on Br^- removal by different SIACs results were presented in Figure 5.8. The DDW was spiked with ~262 ppb initial Br^- and 2.5 mg/L NOM to determine the NOM effect without the interference of any other ions or substances.

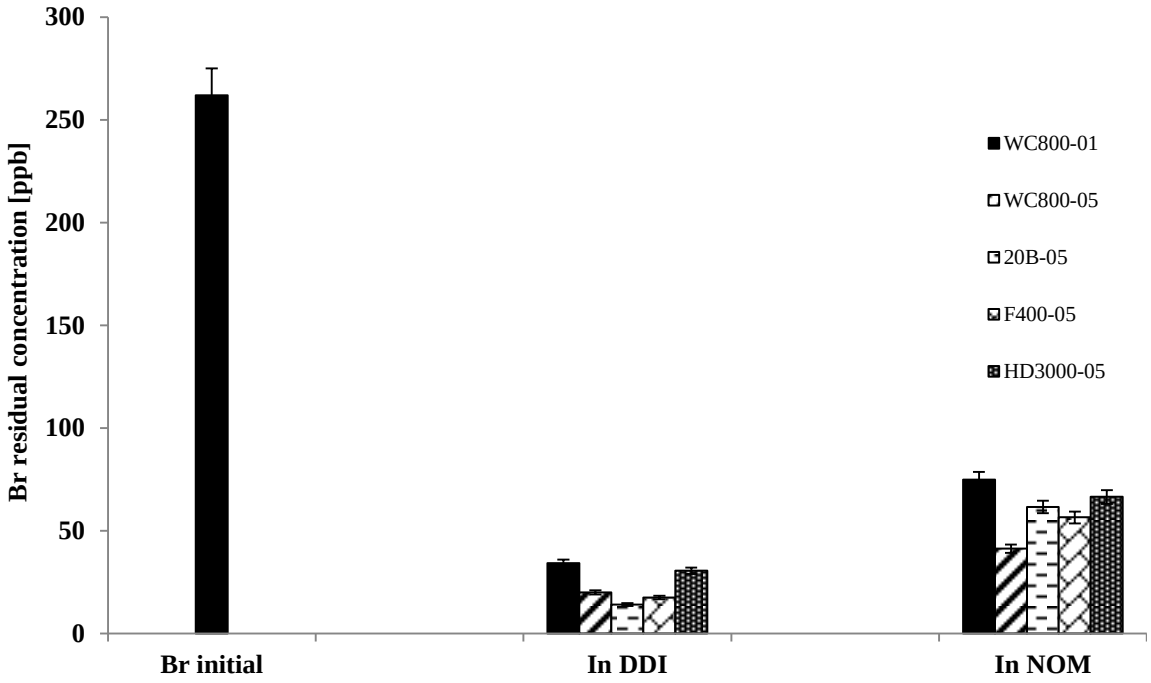

Figure 5.8 Br^- removal by different SIACs in DDW and NOM. All Br^- concentrations reported as mean ± percentage error obtained from duplicates.

Five SIACs were used. Four were prepared with 0.5 M $AgNO_3$ (WC800-05 ox, 20B-05 ox, F400-05 ox, and HD3000-05 ox) and one with 0.1 M $AgNO_3$ (WC800-01 ox). The five SIACs, at 25 mg/L carbon dose, showed about 87% to 95% removal in DDW, but in the presence of 2.5 mg/L NOM isolates, the bromide removal decreased to ~70%

to 84%. There was ~15% decrease in bromide uptake by the same SIACs in the presence of 2.5 mg/L NOM. The tested five SIACs had similar Br^- uptake in DDW, but in NOM, the difference in Br^- removal among them was more distinguishable. The Br^- removal was largely reduced because of NOM competition. The 'Br^- removal' percentage compared to the percentage in DDW was much lower: 20B-05 (18.6% lower) > WC800-01 (15.5% lower) > F400-05 (14.8% lower) > HD3000-05 (14% lower) > WC800-05 (10.4% lower). The NOM had the most influence on 20B-05 ox SIAC, which showed the best Br^- removal in DDW, and the worst Br^- removal in the presence of 2.5 mg/L NOM. The 20B activated carbon was mesoporous (diameter between 2 nm and 50 nm) with the largest surface area, and relatively low silver content (3.6%). Some NOM particle sizes were present in Table 5.4.

Table 5.4 Hydrodynamic diameters (d_h) for NOM

Organic Matter	d_h nm	Reference
Aquatic DOM	< 10	Zanardi-Lamardo et al. (2002)
Aquatic DOM	< 10	Baalousha et al. (2006)
Aquatic FA	1.5-3.0	Man Tang et al. (2001)
Aquatic HA	3.2	ibid
Porewater DOM	1.8	ibid
Groundwater FA	2.1	ibid
Groudwater DOM	2.2	ibid
Groundwater HS	< 3	Gechei et al. (2003)
Aldrich HA	2.6-5.8	Manh Tang et al. (2001); Bouby et al. (2002)
Sediment HS	2-6	Siripinyanond et al. (2006)

Most NOM hydraulic diameters are between 2 nm and 10 nm as shown in table, as a result, most of the NOM substances can enter the mesopores on the activated carbon

surface, which can lead to NOM competition with the Br^- ions for adsorption sites in the carbon mesopores, or even carbon pore blockage. Therefore, among the SIACs tested, NOM competition was most severe in the mesoporous 20B SIAC with largest surface area. The low silver content (3.6%) also decreased the chances of Br^- adsorption by the low concentration of silver species. WC800 and F400 SIACs had more micropores (47% and 62% for WC800 and F400, respectively) (diameter < 2 nm) that only allow Br^- ions to enter, and relatively higher silver contents; therefore, the NOM competition was to some extent reduced.

To investigate the NOM effect in the presence of Cl^-, Br^- adsorption experiments were conducted with 4.03% commercial SIAC in Cl^- spiked water at 50 mg/L carbon dose. The NOM effect on Br^- uptake by SIAC is clearly shown in Figure 5.9.

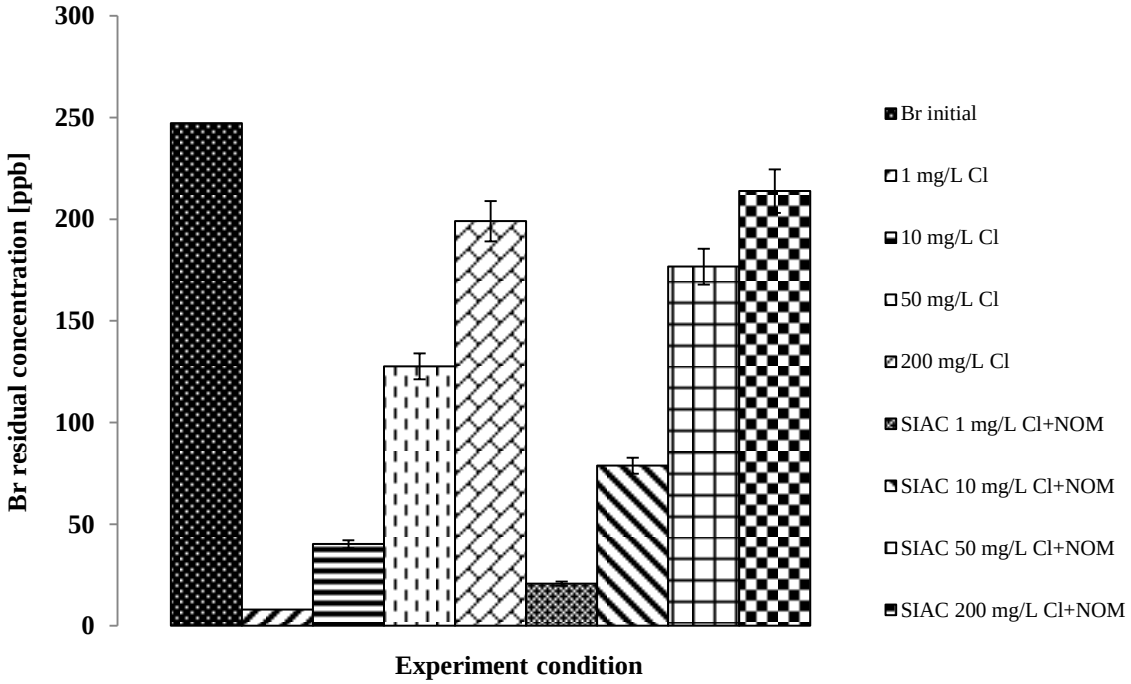

Figure 5.9 Br^- removal by 4.03% SIAC in NOM (2.5 mg/L) and Cl^- spike waters (carbon dose: 50 mg/L). All Br^- concentrations reported as mean ± percentage error obtained from duplicates.

At low Cl^- concentration (1 mg/L), the Cl^- competition effect was not considerable. The NOM effect was the dominant interference on Br^- adsorption; about 5% Br^- removal decrease was observed. As the Cl^- dose increased, the NOM and Cl^- competition worked as a combined interference on Br^- removal. At 10 mg/L Cl^-, the Br^- removal decrease was 14%, while at 50 mg/L Cl^-, the Br^- removal decrease was up to 20%. At very high Cl^- (50 -200 mg/L), the Cl^- competition mechanism dominated the Br^- uptake reduction and resulted in very low Br^- uptake by SIACs with or without presence of NOM.

5.3.3 Effect of Other Anions

Experiments were conducted to examine the effects of other anion competitions on Br^- removal by the SIACs produced in our laboratory. The competition between Br^- and other soluble ions (i.e, NO_3^-/SO_4^{2-}) is shown in Figure 5.10. The NO_3^- and SO_4^{2-} concentrations ranged from 10 mg/L to 100 mg/L. For NO_3^-, at 10 mg/L and 40 mg/L NO_3^- dose, no competition was observed. For SO_4^{2-}, at 10 mg/L SO_4^{2-} dose, no effect was observed; however, at 100 mg/L SO_4^{2-}, there was a notable decrease in the Br^- removal. Even though 100 mg/L SO_4^{2-} dose is high, it has a practical meaning. During the coagulation/ flocculation process, large amounts of coagulant (alum, i.e. $KAl(SO_4)_2 \cdot 12H_2O$) are added. In treated water, the TOC is large decreased, but the SO_4^{2-} concentration is greatly increased.

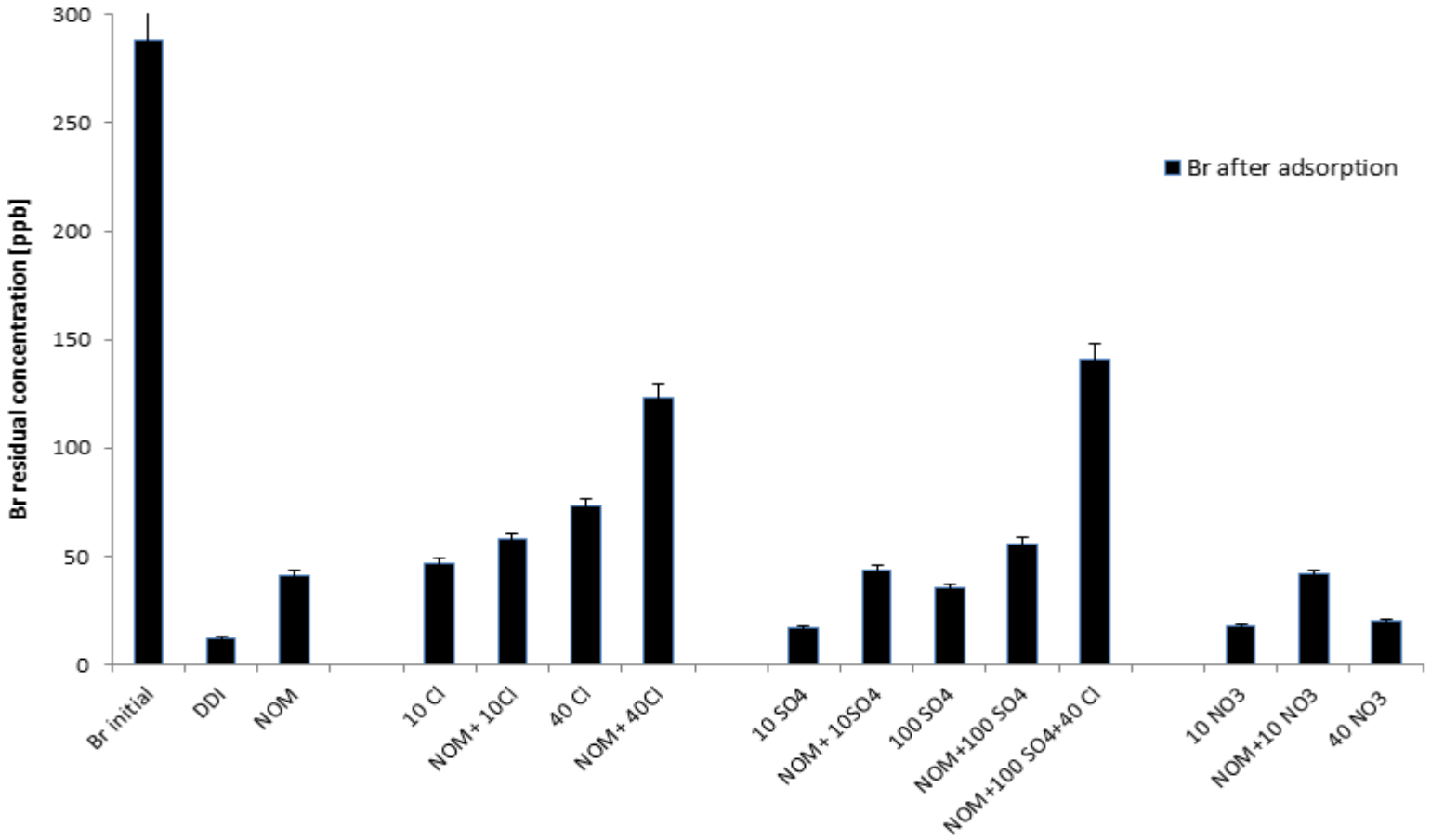

Figure 5.10 Br^- removals by WC800 SIAC in different anions and NOM (2.5 mg/L) spiked waters. All Br^- concentrations reported as mean ± percentage error obtained from duplicates.

5.3.4 The Effect of Source Waters

Bromide removal was assessed in a series of natural water samples to investigate the effectiveness of the SIACs in the background matrix of natural water. The water samples were used as received (raw) and spiked with Br^- to investigate the competition and Br^- removal mechanisms. The water samples were collected from Lake Hartwell, Charleston, Myrtle Beach, Bushypark Reservoir, Broad River and Edisto River. The quality parameters are tabulated in Table 5.5. Water sources were selected to mimic low, medium and high dissolved organic carbon (DOC). The $SUVA_{254}$ values indicated that the organic matter in these sources was from aromatic (high $SUVA_{254}$) to aliphatic (low $SUVA_{254}$) in character. The ion concentrations were elevated for Br^- (300 μg/L), Cl^- (40 mg/L) ions by spiking. The natural water experiments were conducted at four hours contact time.

In order to investigate the background matrix effect in natural waters, WC800-05 ox SIAC was tested in several selected natural waters with different background matrix.

Table 5.5 Selected source water characteristics

	Br^- Concentration ppb	**Cl^- Concentration mg/L**	**SO_4^{2-} Concentration mg/L**	**NO_3^- Concentration mg/L**	**TOC mg/L**	**UV cm^{-1}**	**SUVA**
CH Raw	81	15.3	6.0	0.08	11.8	0.201	1.7
MB Raw	100	19.5	5.7	0.53	27.6	1.203	4.4
CH Treated	81	14.5	35.2	0.09	3.4	0.045	1.3
MB Treated	100	18.3	112.5	0.49	8.3	0.168	2.0
Bushi Park	79.9	29.5	5.7	0.3	4.4	0.170	3.9
Edisto River	33.2	37.9	7.7	0.51	5.0	0.260	5.2
Savanah River	197.5	40.4	10.7	1.04	3.3	0.110	3.3
Lake Hartwell	20.1	2.6	2.0	0.61	2.1	0.038	1.8
Broad River	95	14.3	6.3	0.35	5.4	0.160	3.0

As shown in Figure 5.11, in HW water, with relatively low TOC (2.3 mg/L), low SUVA value (1.83) and low background ions concentrations, the bromide removal by SIAC was up to 53.5%.

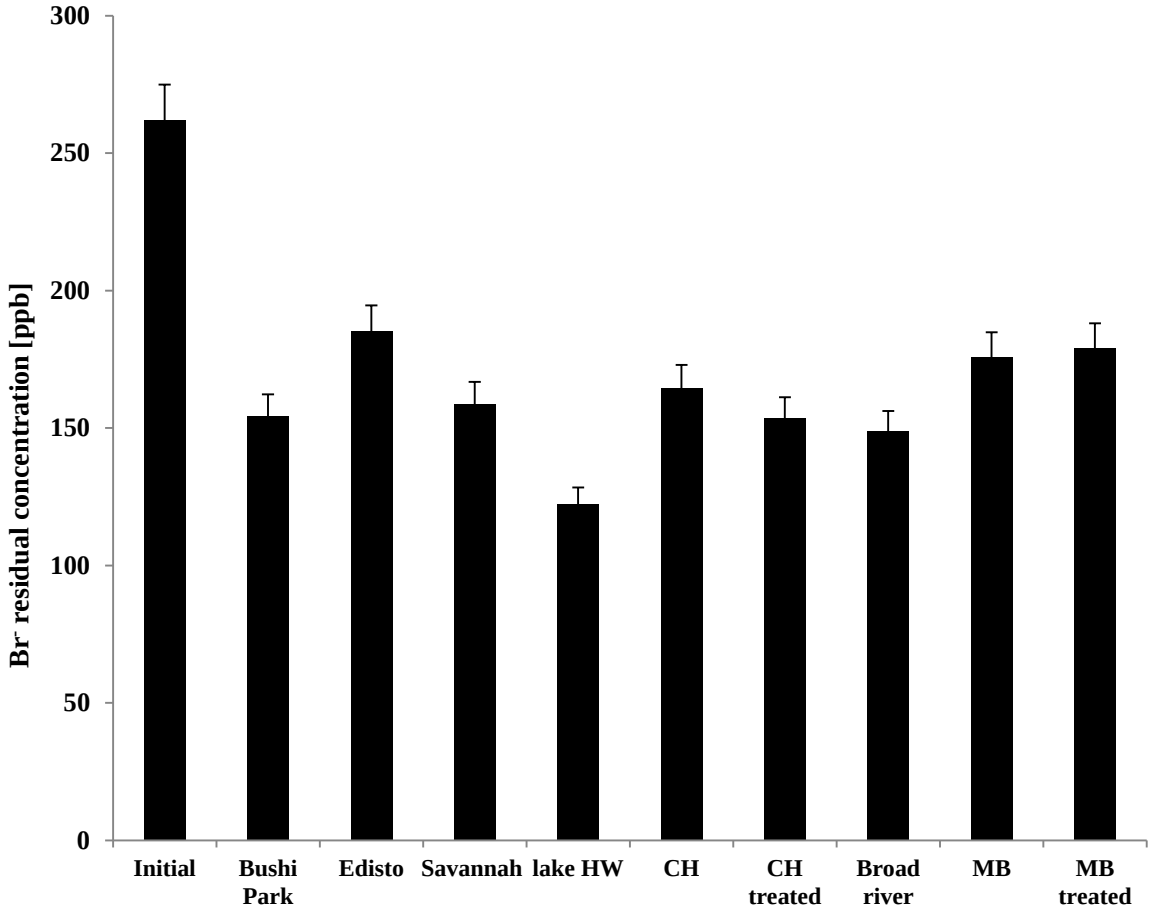

Figure 5.11 Br^- removals by WC800 SIAC in different source waters. All Br^- concentrations reported as mean ± percentage error obtained from duplicates.

When the Cl^- concentration increased to ~15 mg/L level, as in Broad River water and Charleston Water (CH raw and CH treated), the combined interference of Cl^- competition and NOM affected the Br^- adsorption by SIAC, the Broad River water had similar Cl^- concentration to CH raw, but less TOC which resulted in slightly higher Br^- adsorption. The CH treated sample had a similar water characteristics (Cl^- concentration,

TOC, SUVA) to the Broad River, and the Br^- adsorption was similar as expected. As the Cl^- concentration increased from 20 mg/L to 40 mg/L, the Cl^- competition had dominant influence on the Br^- adsorption. At relatively low TOC level, the natural waters with the highest level of Cl^- concentrations still showed lowest Br^- uptakes by SIACs, as was observed in the samples from Bushypark, Edisto, Savannah River, and Myrtle Beach treated water. Furthermore, the Myrtle Beach raw water had very high TOC and high Cl^-, which resulted in low Br^- uptake by the SIAC as expected. While in the Myrtle Beach treated water, more than two thirds of the TOC was removed during the water treatment process, leaving the residual TOC at about 8.3 mg/L. However, the large decrease in TOC did not result in better Br^- uptake. The Cl^- concentration was not reduced in the water treatment, and the high level of Cl^- (20 mg/L) competition affected the Br^- removal. During the water treatment process, a large amount of alum was added in the coagulation/ flocculation process to remove the high level of TOC, which resulted in a high concentration of SO_4^{2-} ions (112 mg/L) in the Myrtle Beach treated water, the very large amount of SO_4^{2-} might interfere with Br^- adsorption by SIAC.

5.3.5 The Effect of Alum Coagulation

Activated carbon was typically added to water before or after coagulation/flocculation during water treatment [Kristiana et al., 2011]. Jar test experiment was conducted with 4.03% SIAC, the coagulant (i.e. alum) dose was 30 mg/L, the natural water was Broad River water, and the F400 carbon with no silver attached was for comparison. The SIAC dose ranged from 10 mg/L, 25 mg/L to 50 mg/L, the initial pH of Broad River water was 7.28, which decreased to 6.48 after 30 mg/L alum was added. The pH remained unchanged during the rapid and slow mixing. The rapid mixing was achieved by a motor rotating at 200 rpm for 1 minute, while slow mixing at 25 rpm for 20 min, the settling down time was 2 hours. The total detention time of the jar test experiment of 4.03% SIAC was 140 minutes. Eight jars were used to investigate the bromide removal effect of 30 mg/L alum alone; 50 mg/L F400 PAC with no silver; various SIAC doses with no alum added (10 mg/L, 25 mg/L, 50 mg/L), and various SIAC dose with 30 mg/L alum added (10 mg/L, 25 mg/L, 50 mg/L).

The jar test results are presented in Figure 5.12. Alum alone was not able to remove Br^- from aqueous solution. F400 carbon with no silver impregnated was not able to remove Br^-. Larger amount of Br^- removal was observed at higher SIAC dose. The Br^- removal by SIAC was 30- 40% and alum did not make a notable difference. The alum did not remove Br^-, and no considerable difference of Br^- removal was observed with or without alum added. The ‘flocs’ formed during the coagulation did not have negative effect on the Br^- uptake by SIACs. Therefore, coagulation in the jar test was shown to have no considerable effect on Br^- removal.

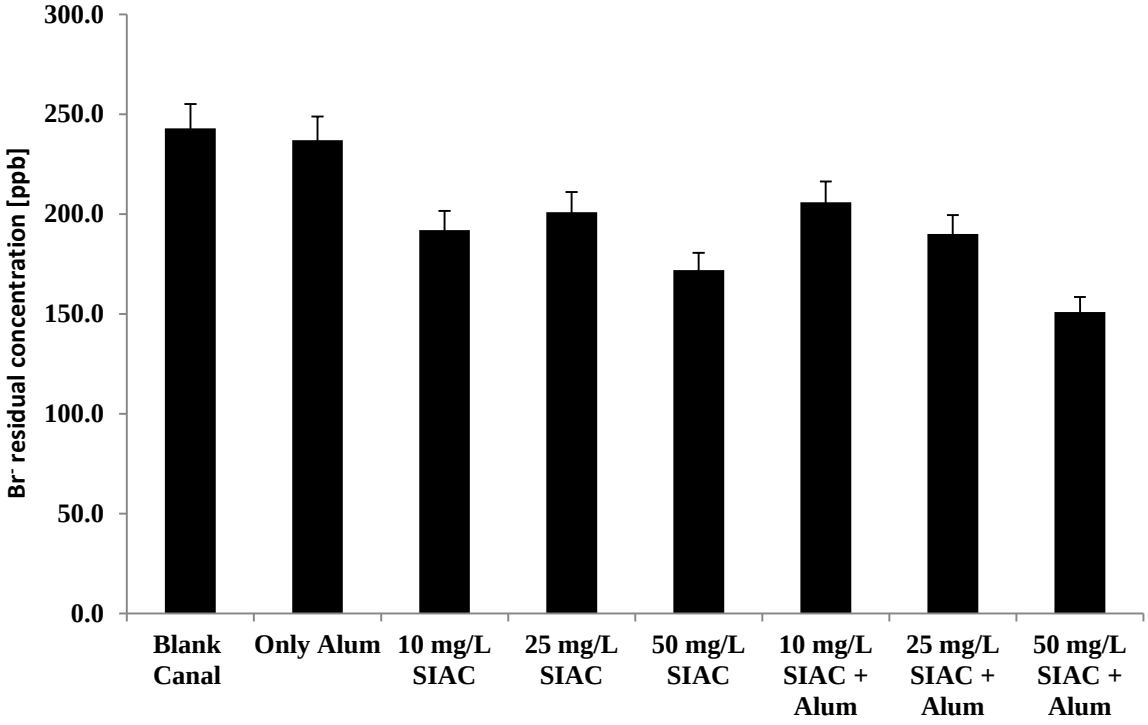

Figure5.12 Alum coagulation effect on Br^- removal by 4.03% SIAC in jar test All Br^- concentrations reported as mean ± percentage error obtained from duplicates.

5.4 The Application of SIACs for THM Control

Bromide is an important DBPs precursor (e.g. brominated THM precursor), as discussed in previous chapter. In this study, experiments were conducted to investigate the effect of removing bromide from natural waters on the DBPs (i.e. THM) formation in the SIAC treated waters. THMs are a group of four chemicals that are formed along with other disinfection byproducts when chlorine or other disinfectants used to control microbial contaminants in drinking water react with naturally occurring organic and inorganic matter in water. The THMs are: chloroform (TCM), bromodichloromethane (DCBM), dibromochloromethane (DBCM), and bromoform (TBM). USEPA has

published the Stage 1 Disinfectants/Disinfection Byproducts Rule to regulate total trihalomethanes (TTHM) at a maximum allowable annual average level of 80 ppb.

To investigate the effect of Br^- removal by SIACs on THM formation, the THMs formation experiments (per the uniform formation condition (UFC) protocol) were conducted to determine how the addition of SIACs assist with the control of brominated DBPs formation.

The Br^- adsorption effect on THM formation control experiment results are shown in Figures 5.14 to 5.18. From the Br^- removal experiment results presented in Figure 5.13, it is clear that in NOM+ 40Cl, HW raw, and HW+ 40Cl waters, large amounts of Br^- were removed from aqueous condition, the Br^- removal percentages were ~ 52.6%, 67.4% and 39.0%, respectively. The Br^- initial was spiked to ~290 ppb, Br^- adsorption experiments were done with WC-800 low T ox SIACs.

The THM formation and speciation results were summarized in Table 5.6. As shown in Figure 5.14, in the raw waters with no bromide spike, the overall THM formation in NOM+40Cl, HW raw and HW+40Cl were 72, 33, 32 µg/L, respectively. The major THM speciation was TCM (from 75% to 90%), as the bromide concentration was low in each water (0 ppb in NOM+40Cl, 20 ppb in HW). But when spiked with 300 ppb Br^-, the THM formation speciation largely shifted from TCM to DCBM, DBCM, and TBM, and the overall THM formation was greatly increased (see Figure 5.15). For NOM+40Cl, the overall THM formation increased from 72 µg/L to 122 µg/L. About 114 µg/L of the brominated THMs were created after disinfection as a result of spiking 300 µg/L Br^- into water. Up to 93.4% of total THM were brominated species. For HW raw

water, after Br^- spiking, the overall THM formation increased from 33 µg/L to 76 µg/L. About 69 µg/L (90.7% of total THMs) of the brominated THMs were created. For HW+40Cl water, after Br^- spiking, the overall THM formation increased from 32 µg/L to 70 µg/L, about 64 µg/L (91.4% of total THMs) of the brominated THMs were created. As shown in Figure 5.16, after SIACs adsorption, the Br^- residual concentration in NOM+40Cl, HW raw, HW+40Cl, decreased from 300 µg/L to 138.1 µg/L, 95.2 µg/L and 177.1 µg/L, respectively. Accordingly, because the DBP precursor Br^- was removed, the THM formation was largely decreased. In NOM+40Cl after SIAC treated, the brominated THMs concentration decreased from 114 µg/L to 55 µg/L (shown in Figure 5.16). In HW raw after SIAC treated, the brominated THMs decreased from 69 µg/L to 30 µg/L (shown in Figure 5.17). In HW+40Cl after SIAC treated, the brominated THMs decreased from 64 µg/L to 37 µg/L (shown in Figure 5.18). The dramatic reduction of brominated THM formation was attributed to the Br^- (THM precursor) adsorption by SIACs. Another important precursor, natural organic matter, was also measured before and after SIAC treatment, very limited TOC reduction was observed, as is shown in Table 5.6. Therefore, the large Br^- removal realized by SIAC adsorption played an important role in THMs formation control, especially for the control of brominated THM formation. As described in previous chapter, the brominated DBPs are more cyto- and geno- toxic than the chlorinated form. This SIAC adsorption approach provides a novel and effective way of controlling brominated DBPs formation, and is of great importance especially for waters with bromide spiking issues.

Table 5.6 THM formation and speciation results

	THM µg/L	TCM µg/L	DCBM µg/L	DBCM µg/L	TBM µg/L	TOC mg/L
NOM+40Cl	72	64	8	0	0	2.2
NOM+40Cl Br spiked	122	8	42	56	17	2.2
NOM+40Cl after adsorption	63	8	31	21	3	1.9
HW raw	33	26	6	1	0	1.7
HW raw Br spiked	76	7	13	28	28	1.7
HW raw after adsorption	39	9	11	13	6	1.5
HW+40Cl	32	24	6	2	0	1.6
HW+40Cl Br spiked	70	6	14	27	23	1.6
HW+40Cl after adsorption	43	6	10	15	12	1.4

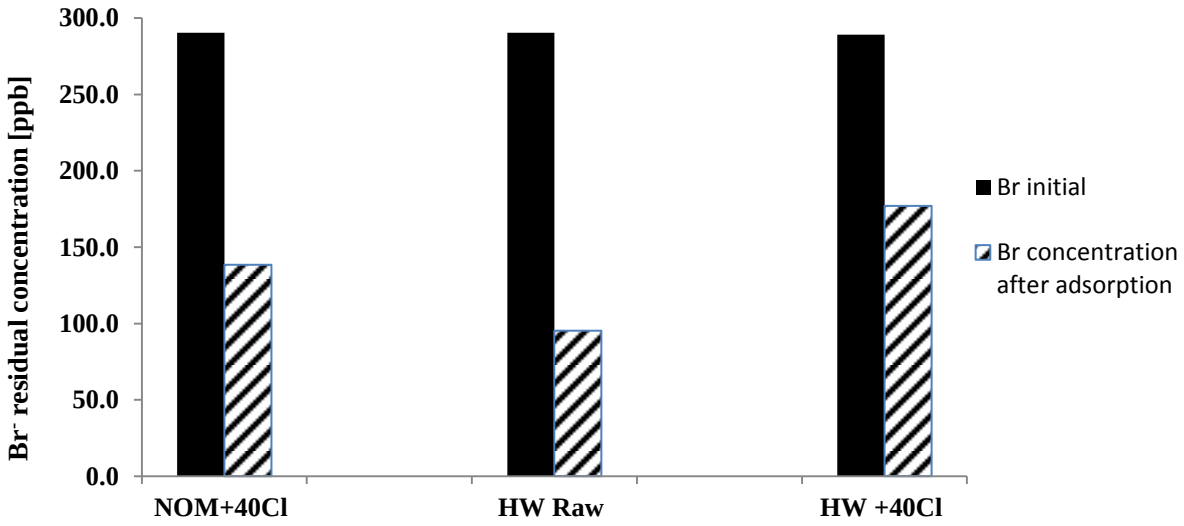

Figure 5.13 Br^- removals by WC800 low T ox SIAC in NOM and HW with Cl^- spiked waters (2.5 mg/L NOM, the WC800 low T ox SIAC dose was 25 mg/L)

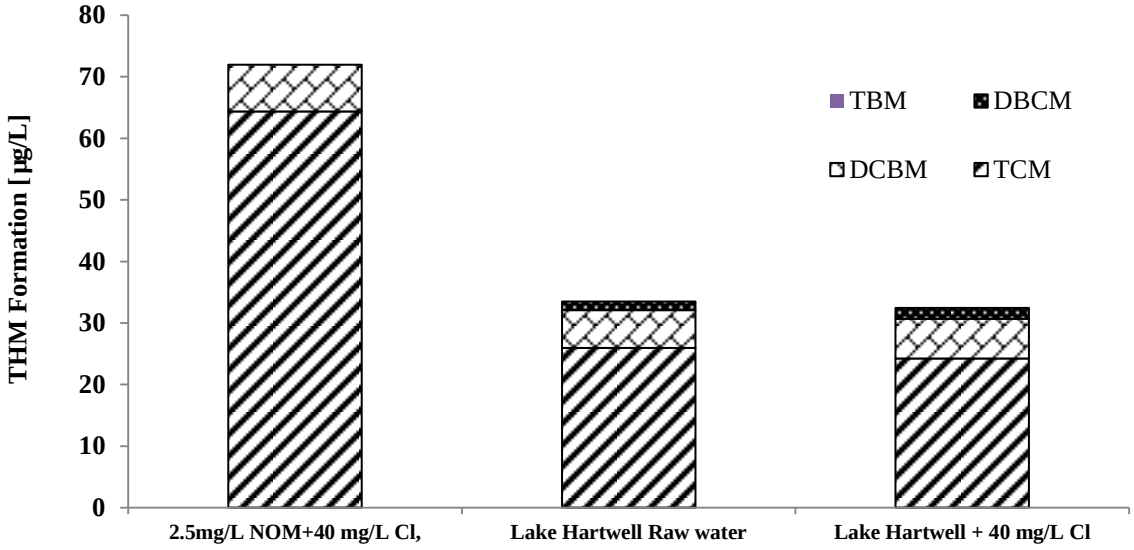

Figure 5.14 THM formation and speciation Raw waters

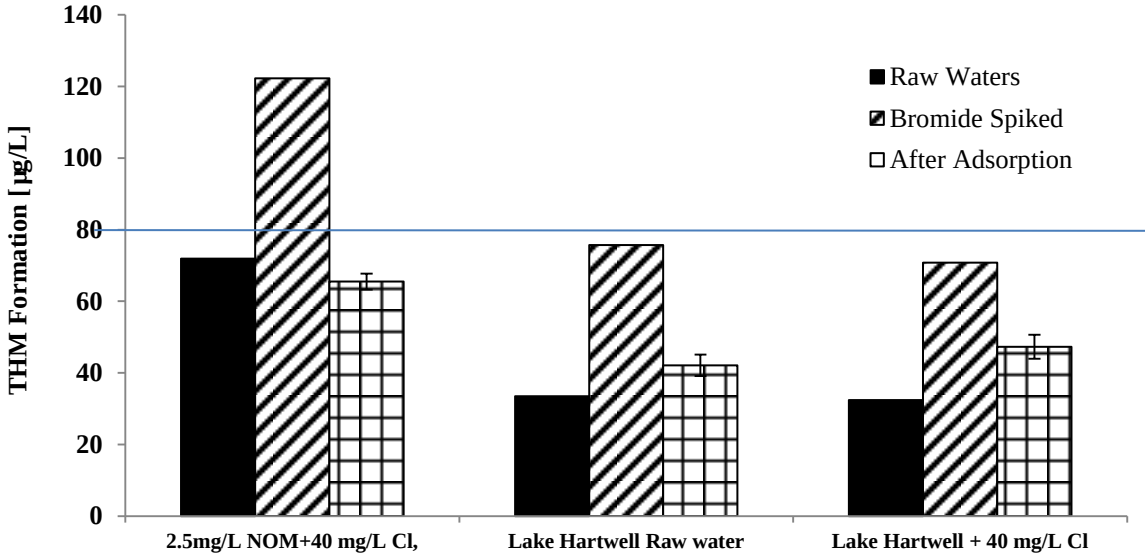

Figure 5.15 Overall THM formation in raw, Br^- spiked, and SIAC treated waters. The line showed the maximum contaminant level (MCL) was 80 µg/L of THMs by USEPA.

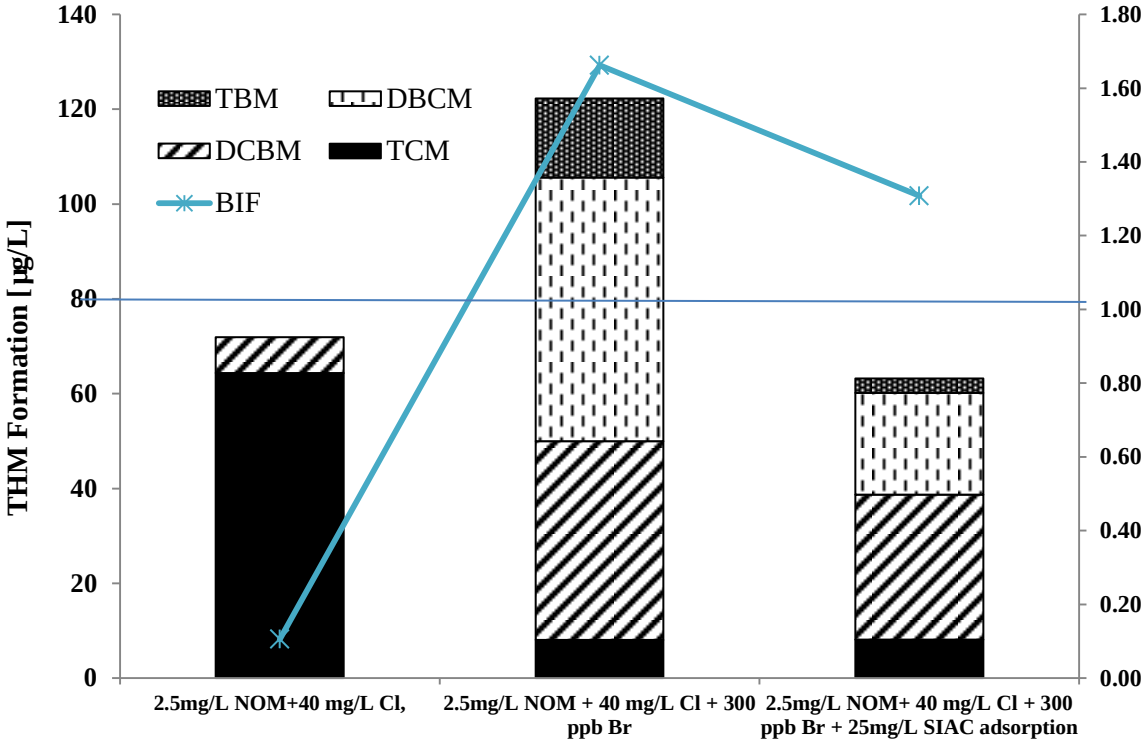

Figure 5.16 THM formation and speciation in NOM+40Cl water (note: BIF was the bromine incorporation factor)

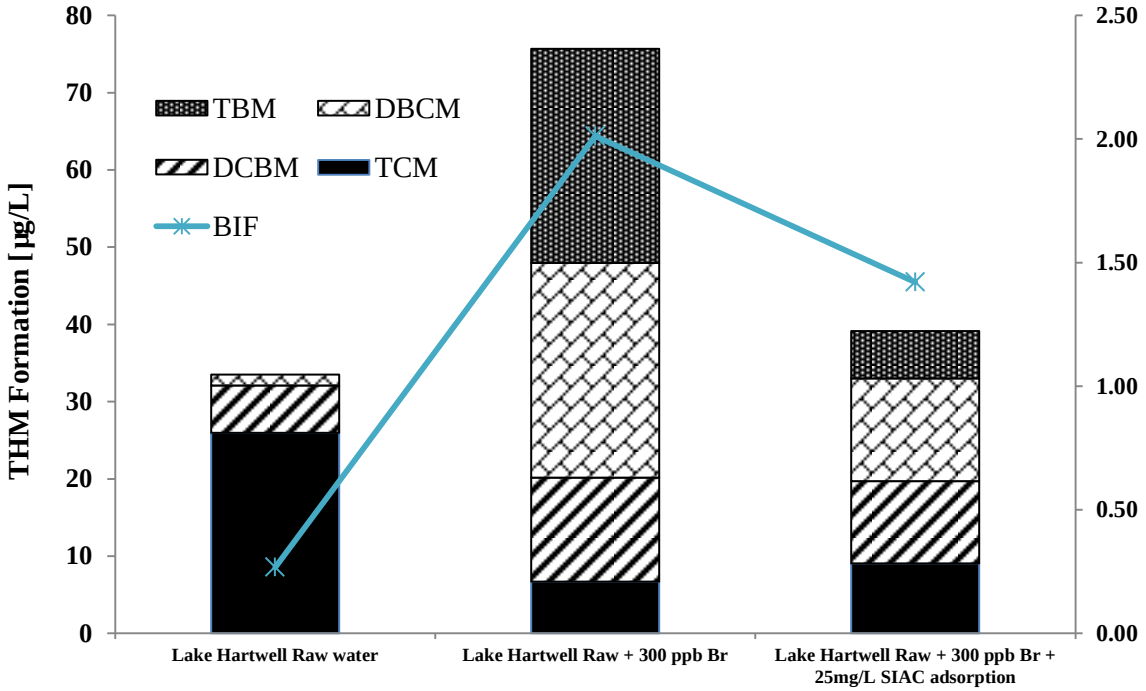

Figure 5.17 THM formation and speciation in Lake HW raw

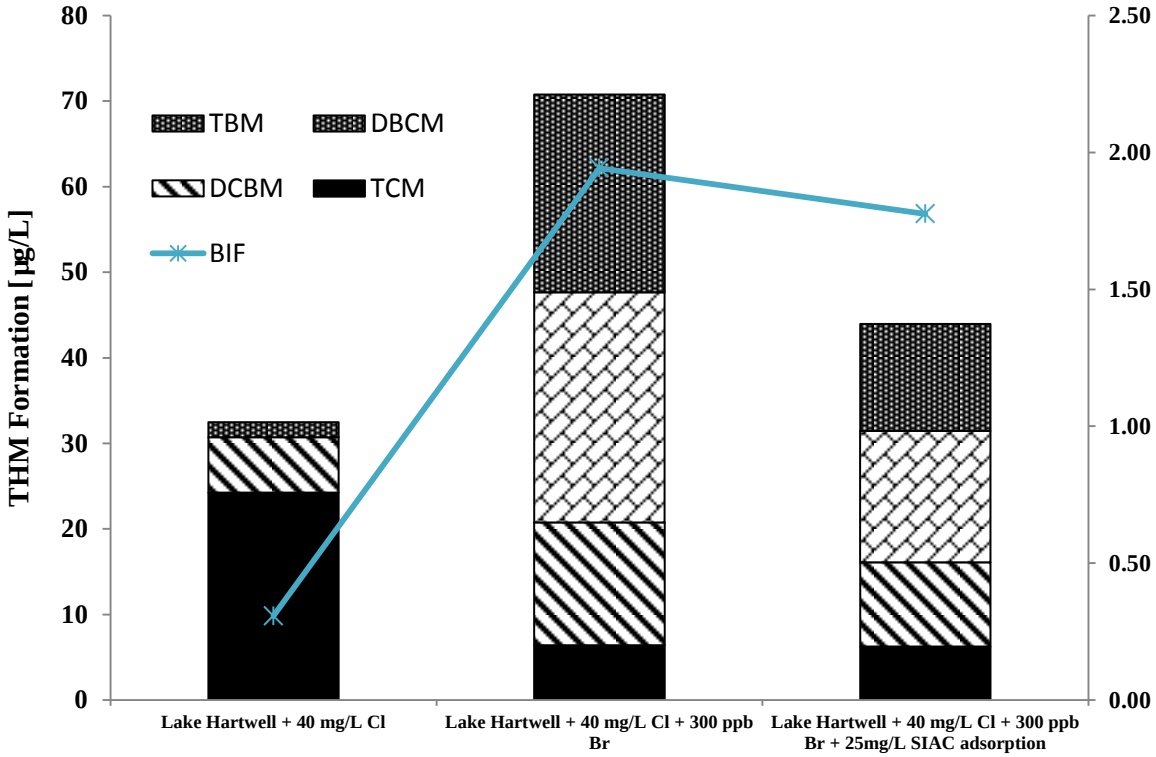

Figure 5.18 THM formation and speciation in HW + 40 Cl

CHAPTER 6 CONCLUSIONS AND RECOMMENDATIONS

The major conclusions obtained from this study are summarized as follows

Objective (1): to determine the optimum silver impregnation protocols and assess the role of carbon characteristics (e.g., activated carbon characteristics, silver impregnation techniques and pre-oxidation conditions) to produce SIACs to remove Br^- from natural waters; and evaluate their effectiveness for Br^- removal.

- Generally, SIACs with higher SSAs showed better Br^- removal in DDW.
- PAC pre-oxidation by 15.7N HNO_3 at 90℃ heating temperature was found to be appropriate, 0.5M is appropriate $AgNO_3$ concentration for silver impregnation process.
- Relatively higher oxygen content (an indication for presence of new oxygen-containing functionalities) and smaller SSA were observed after PAC oxidation; the severity of oxidation was influenced by both of oxidant concentration and oxidation temperature, among which the oxidation temperature was more influential on PAC characteristics.
- SIACs with pre-oxidation showed better Br^- uptake than SIACs with no pre-oxidation.
- SIACs impregnated at higher $AgNO_3$ concentration showed better Br^- removal.
- There was a negative correlation (R= 0.8) better silver content and SSAs of SIACs.

Objective (2): to evaluate the developed SIACs at typical water treatment conditions. This task involved mainly investigating the competing anions (e.g. Cl-) and NOM and the background matrix effect in natural water samples (e.g. pH, TOC, SUVA, presence of alum during coagulation/flocculation, etc.)

- There was a decrease in Br^- removal with increasing dose of Cl^- due to Cl^- competition. The Cl^- and Br^- compete for the carbon pores and active adsorption sites.
- Under the same conditions and same SIAC dose, the Cl^-: Br^- ratio played an important role in the Br^- removal, the lower the Cl^-: Br^- ratio, the higher the Br^- removal can be achieved by the SIACs.
- Presence of NOM decreased Br^- removal; this decrease was attributed to pore blockage and NOM competition.
- Mesoporous SIACs are more likely to be influenced by NOM competition, because the carbon mesopore size is similar to NOM size (2 nm to 50 nm).
- The Br^- removal by SIAC in HW was up to 56%, but was largely decreased (only ~30% removal) in high Cl^- (~40 mg/L) concentration and high TOC (27 mg/L) source waters.
- The Cl^- and NOM competition work as a combined interference for Br^- removal by SIACs.
- According to the jar test results, alum was not able to effectively remove bromide from water. Virgin activated carbon was not able to effectively remove bromide from water. At two hours retention time (to mimic the real coagulation/flocculation

process), Br^- removal by SIAC was 30- 40% in jar test and alum did not make a notable difference.

Objective (3): to evaluate the impact of selected SIAC for DBPs formation control (i.e., THMs control) in natural waters.

- Br^- spiking largely shifted the THM species from chlorinated to brominated species, and the overall THM formation was increased.
- The large Br^- removal by SIAC adsorption played an important role in THMs formation control, especially for the control of brominated THM formation.

RECOMMENDATIONS

Some recommendations for application and future research are listed below:

- Due to the low solubility product of Ag_3PO_4 (Ksp $Ag_3PO_4 = 8.9*10^{-17}$, Ksp AgBr = $5.2*10^{-13}$), another potential competitive anion in water is PO_4^{3-}, although at low concentrations in nature (< 100 µg/L), further experiment is recommended to investigate the anion competition effect between PO_4^{3-} and Br^-.
- Investigating the ionic strength effect of the background water may be useful in understanding how the soluble ions in the background water can influence the Br^- adsorption by SIACs.
- Select more types and more concentrations of NOMs to help understanding the NOM effect on Br- adsorption by SIAC.
- Rapid small-scale column tests are recommended to create a representative breakthrough profile for the SIACs.
- Conducting jar test for the most promising SIACs is recommended. Because SIACs are meant to be added before or after coagulation/flocculation during water treatment (with alum added), the jar test can mimic the real water treatment process and give the results most close to real situations.
- To further determine how the addition of SIACs assist with the control of brominated DBPs formation, conducting I-THM, HAA formation experiments (per the uniform formation condition (UFC) protocol) in natural waters before and after SIACs treatment is recommended.

- Pore-size distribution, SEM, EDX, and XRD measurements are needed in the future to better determine the changes in the physical and chemical properties of SIACs as compared to the virgin ACs, and create a full data base of the SIAC carbon characteristics.
- Iodide ions (I^-) adsorption experiments by SIACs should also be conducted in the future to investigate the performance of I^- removal by SIACs used in this research.

APPENDIX A

Preparation of Silver Chloride Impregnated Activated Carbon

Thirty grams of SIAC (1.05% commercial SIAC and 4.03% commercial SIAC) were packed in low-pressure glass column. One hundred milliliters of 0.1 M HCl (pH=1) was cycled through the column using a peristaltic pump for 5 days in a batch mode (see Figure 4.1). After HCl treatment, the newly produced SIAC-Cl was rinsed with deionized water until the rinsed DDW pH kept constant, and no silver detected by the silver probe. After rinsing, the SIAC-Cl was removed from the column and air-dried in oven at 65 ℃ for 24 hours. The air-dried SIAC-Cl was then dried in vacuum oven overnight. After cooling down in the desiccator, the SIAC-Cl was stored in a sealed container. The 2 M HCl solution used to prepare the carbon and the rinse DDW are collected in beakers and analyzed for silver content using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Figure A-1 Chlorination of SIAC apparatus configuration

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